JOURNAL OF
Materials
CHEMISTRY

Synthesis and characterisation of a conjugated reactive mesogen

Andreas Bacher,[a] Philip G. Bentley,[b] Donal D. C. Bradley,[a] Louise K. Douglas,[a] Paul A. Glarvey,[b] Martin Grell,[a] Katherine S. Whitehead[a] and Michael L. Turner*[b]

[a]Department of Physics and Astronomy, University of Sheffield, Sheffield, UK S3 7RH
[b]Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF

Received 5th August 1999, Accepted 30th September 1999

The synthesis of 2-methyl-1,4-bis[2-(4-propionyloxypropyloxyphenyl)ethenyl]benzene (**1**) and 2-methyl-1,4-bis[2-(4-acryloyloxypropyloxyphenyl)ethenyl]benzene (**2**) is reported. The liquid crystalline and photophysical behaviour has been investigated. Two liquid crystalline phases can be detected, with the lower temperature phase exhibiting strong H-aggregation. Thin films of the reactive mesogen in its liquid crystalline phase can be aligned into monodomains and can be polymerised in a controlled manner to give intractable anisotropic networks.

Introduction

The engineering of new electronic and photonic devices requires materials with unique properties. Organic materials are becoming increasingly important sources of these materials. Three key advantages of molecular semiconductors over their conventional solid state inorganic materials are: processability from solution, chemical bandgap tuning and the development of order at the molecular level. The first two advantages are now widely exploited,[1] but the third has yet to receive more attention. One area where the use of self-organising materials for organic optoelectronics is comparatively advanced is the field of polarised electroluminescence (EL). A number of approaches towards polarised EL have been investigated, for a review see ref. 2. The most advanced polarised EL devices reported so far are based on the self organisation of conjugated liquid crystalline polymers.[3–6] Polarised light sources have tremendous potential as backlights for liquid crystal (LC) displays.

Reactive mesogens (RMs) are low molecular mass LC materials which possess reactive functional groups at their periphery. The LC phases have low viscosity and hence, can be aligned into a monodomain with ease. Crosslinking of the reactive groups in the LC phase produces solid, intractable networks, usually with the help of a photoinitiator. The RM concept has been developed over the past decade[7] and has resulted in remarkable passive optical devices.[8] The state of the art for using RMs for polarised emission is the copolymerisation of fluorescent chromophores into a reactive mesogen matrix.[9] However, due to the lack of suitable material no polarised electroluminescent devices based on conjugated reactive mesogens have yet been reported.

Conjugated RMs promise to be particularly useful for polarised EL devices with multilayer architectures. Since the work of Tang and van Slyke,[10] it is widely acknowledged that multilayer device architectures can improve device performance drastically by allowing for easier and better balanced injection of holes and electrons.

As a first step in applying the RM concept to polarised EL applications, we report here on the synthesis and characterization of conjugated reactive mesogens with a substituted distyrylbenzene as the mesogenic core. Oligomers with *p*-(phenylenevinylene) units like distyrylbenzene are well known to exhibit strong fluorescence.[11]

Experimental

^{1}H- and ^{13}C-NMR spectra were obtained using a Bruker AC250 NMR spectrometer equipped with an autosampler. Deuterated chloroform was used as the solvent unless otherwise stated. Thermal properties under a nitrogen atmosphere were determined by DSC using a Perkin-Elmer Pyris 1 calibrated using an indium standard. The heating and cooling rates in all cases were 10 °C min^{-1}. Polarised light microscopy was carried out with an Olympus BH-2 optical microscope equipped with a Linkam THM600 hotstage and a PR600 control unit. Liquid crystal testing cells for homogeneous alignment with a film thickness of 7 μm were supplied by E.H.C. Ltd. of Tokyo, Japan. These cells allowed the application of a voltage across the film. Absorption spectra were recorded on a Unicam UV/Vis 4 spectrophotometer. For polarised absorption spectroscopy, a Glan-Thomson polariser was inserted into the sample beam, and a baseline was recorded before every sample scan to compensate for the polarisation bias of the instrument. PL spectra were taken with a Perkin-Elmer LS-5 luminescence spectrometer. Thin films were spin coated from a 30 g l^{-1} solution in THF at 1500 rpm. Thermal crosslinking of these films was carried out in a nitrogen purged Linkam hotstage. Liquid crystalline alignment layers were prepared from the commercial alignment layer kit MERCK ZLI 2650.

Preparation of 4-(hydroxypropyloxy)styrene

4-Acetoxystyrene (5 g, 30 mmol) and KOH (2.15 g, 38 mmol) were dissolved in ethanol (100 ml), placed under nitrogen and stirred at room temperature for 1 h. Sodium ethoxide (2.5 g, 37 mmol) was then added and the temperature was raised to reflux. After 1 h a solution of 3-bromopropanol (4 g, 29 mmol) in ethanol (100 ml) was added over 30 min and the reaction mixture stirred for 24 h. The solvent was evaporated under reduced pressure and the resulting solid was dissolved in $NaHCO_3$ solution and extracted with DCM (3 × 50 ml). The combined organic phases were dried over $MgSO_4$, evaporated under reduced pressure and recrystallised from hexane. Yield 3.0 g, 58%.

^{1}H-NMR [ppm]: δ 2.04 (CH_2, p, $J = 6$ Hz, 2H), 3.86 (CH_2OH, t, $J = 6$ Hz, 2H), 4.12 (CH_2O, t, $J = 6$ Hz, 2H), 5.12 (=CH_2, dd, $J = 1$, 11 Hz, 1H), 5.61 (=CH_2, dd, $J = 1$, 18 Hz, 1H), 6.65 (C*H*=, dd, $J = 11$, 18 Hz, 1H), 6.86 (Ph, d, $J = 9$ Hz, 2H), 7.34 (Ph, d, $J = 9$ Hz, 2H).

Preparation of 4-(3-propionyloxypropyloxy)styrene

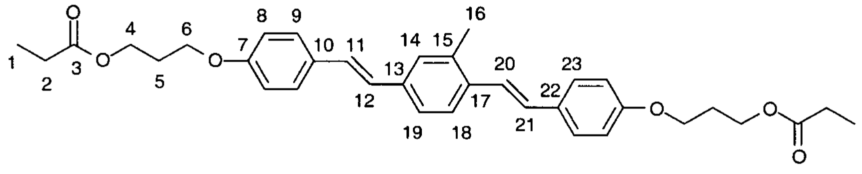
4-(Hydroxypropyloxy)styrene (2.8 g, 15.9 mmol) and triethylamine (1.16 ml, 27 mmol) were suspended in 100 ml of dry DCM and cooled to 0 °C. Propionyl chloride (1.46 ml, 17.5 mmol) in 30 ml of DCM was then added over 10 min, the resulting mixture was allowed to warm to room temperature and stirred for 1 h before being poured into 2% HCl solution. This mixture was extracted with DCM (3 x 50 ml), washed with 2% HCl solution (2 x 50 ml), water (50 ml), and dried over $MgSO_4$ before purification by eluting though a short silica column. Yield 3.5 g, 94%.

^1H-NMR [ppm]: δ 1.13 (Me, t, $J=8$ Hz, 3H), 2.11 (CH_2, p, $J=6$ Hz, 2H), 2.33 (CH_2Me, q, $J=8$ Hz, 2H), 4.04 ($CH_2OC(O)$, t, $J=6$ Hz, 2H), 4.26 (CH_2O, t, $J=6$ Hz, 2H), 5.12 ($=CH_2$, dd, $J=1$, 11 Hz, 1H), 5.60 ($=CH_2$, dd, $J=1$, 18 Hz, 1H), 6.65 ($CH=$, dd, $J=11$, 18 Hz, 1H), 6.84 (Ph, d, $J=9$ Hz, 2H), 7.33 (Ph, d, $J=9$ Hz, 2H).

Preparation of 2-methyl-1,4-bis[2-(4-propionyloxypropyloxyphenyl)ethenyl]benzene (1)

4-(3-Propionyloxypropyloxy)styrene (3.48 g, 13.2 mmol), 2,5-dibromotoluene (1.5 g, 6 mmol), triethylamine (1.82 g, 2.50 ml, 18 mmol), DMF (50 ml) and palladacycle catalyst[14] (40 mg, 0.7 mol%) were placed in a 100 ml flask and thoroughly degassed with nitrogen. The mixture was then heated to 125 °C for 5 h, cooled, poured into 2% HCl solution and extracted with DCM (3 x 50 ml). The organic fractions were combined and washed with 2% HCl solution (4 x 50 ml), 2% NaOH solution (50 ml), water (2 x 50 ml), dried over $MgSO_4$ and the solvent removed under reduced pressure. The bright yellow powder was redissolved in DCM and passed through a short column of Celite, the solvent removed and the product **1** recrystallised from isopropanol. Yield 1.8 g, 54%.

^1H-NMR [ppm]: δ 1.14 (CH_2Me, t, $J=8$ Hz, 6H), 2.13 ($CH_2CH_2OC(O)$, p, $J=6$ Hz, 4H), 2.34 (CH_2Me, q, $J=8$ Hz, 4H), 2.42 (PhMe, s, 3H), 4.07 ($CH_2CH_2OC(O)$, t, $J=6$ Hz, 4H), 4.28 (OCH_2, t, $J=6$ Hz, 4H), 6.87 (Ph, d, $J=9$ Hz, 2H), 6.88 (Ph, d, $J=9$ Hz, 2H), 6.93 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 6.97 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 7.06 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 7.18 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 7.29 (PhMe, d, $J=2$ Hz, 1H), 7.33 (PhMe, dd, $J=2$, 8 Hz, 1H), 7.44 (Ph, d, $J=9$ Hz, 2H), 7.45 (Ph, d, $J=9$ Hz, 2H), 7.57 (PhMe, d, $J=8$ Hz, 1H).



^{13}C-NMR [ppm]: δ 9.1 (C^1), 20.1 (C^{16}), 27.6 (C^2), 28.7 (C^5), 61.4 (C^4), 64.4 (C^6), 114.7 (C^8), 124.1 (C^{20}), 124.1 (C^{19}), 125.3 (C^{14}), 126.5 (C^{11}), 127.7 (C^9), 127.7 (C^{12}), 127.8 (C^{23}), 128.4 (C^{18}), 129.0 (C^{21}), 130.5 (C^{10}), 130.7 (C^{22}), 135.6 (C^{13}), 135.8 (C^{17}), 136.5 (C^{15}), 158.4 (C^7), 169.0 (C^3).

High-resolution mass spectrometry for $C_{35}H_{40}O_6$: calculated 556.282489, found 556.282874.

Preparation of 2-methyl-1,4-bis[2-(4-acryloyloxypropyloxyphenyl)ethenyl]benzene (2)

Deprotection was carried out by dissolution of **1** (0.9 g, 1.7 mmol) and KOH (0.38 g, 6.8 mmol) in 100 ml of absolute ethanol, followed by heating at reflux for 1 h. After cooling the reaction mixture was washed three times with water and once with acetone. After drying the resulting 2-methyl-1,4-bis[2-(4-hydroxypropyloxyphenyl)ethenyl]benzene (264 mg, 0.5 mmol) was suspended without further purification in DCM (5 ml) under an inert atmosphere and triphenylphosphine (524 mg, 2 mmol) and acrylic acid (0.1 ml, 1.5 mmol) added. The solution was cooled to 0 °C and diethyl azodicarboxylate (DEAD) (0.32 ml, 2 mmol) was added dropwise over 2 min. The resulting mixture was allowed to warm to room temperature and was stirred for 18 h. The mixture was then taken up in DCM (45 ml), washed with $NaHCO_3$ (3 x 30 ml), water (2 x 30 ml), and the organic layer dried with $MgSO_4$. The solvent was removed *in vacuo* and the residue purified by column chromatography (silica gel, eluent DCM). The product **2** was recrystallised from ethanol—yield 197 mg, 62%.

^1H-NMR [ppm]: δ 2.17 ($CH_2CH_2OC(O)$, p, $J=6$ Hz, 4H), 2.44 (PhMe, s, 3H), 4.08 ($CH_2OC(O)$, t, $J=6$ Hz, 4H), 4.37 (OCH_2, t, $J=6$ Hz, 4H), 5.83 ($CH=CH_2$, dd, $J=2$, 10 Hz, 2H), 6.13 ($CH=CH_2$, dd, $J=10$, 17 Hz, 2H), 6.42 ($CH=CH_2$, dd, $J=2$, 17 Hz, 2H), 6.87 (Ph, d, $J=9$ Hz, 2H), 6.88 (PhMe, d, $J=9$ Hz, 2H), 6.93 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 6.97 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 7.06 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 7.18 (PhCH=CHPhMe, d, $J=16$ Hz, 1H), 7.29 (PhMe, d, $J=2$ Hz, 1H), 7.33 (PhMe, dd, $J=2$, 8 Hz, 1H), 7.44 (Ph, d, $J=9$ Hz, 2H), 7.45 (Ph, d, $J=9$ Hz, 2H), 7.57 (PhMe, d, $J=8$ Hz, 1H).

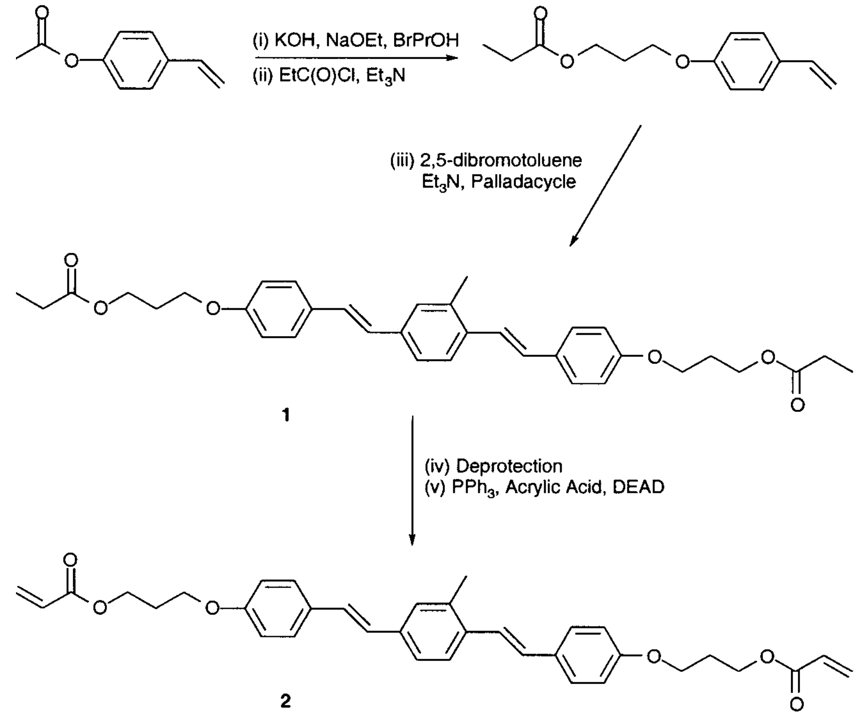
^{13}C-NMR [ppm]: same as **1** except resonances for C^1, C^2, and C^3 are absent and resonances for the acryloyl groups are observed at δ 128.4 ($CH_2=CHC(O)$), 130.9 ($CH_2=CHC(O)$), and 166.2 ($CH_2=CHC(O)$).

High-resolution mass spectrometry for $C_{35}H_{36}O_6$: calculated 552.251189, found 552.253470.

Results and discussion

The conjugated reactive mesogen, 2-methyl-1,4-bis-[2-(4-acryloyloxypropyloxyphenyl)ethenyl]benzene (**2**), was synthesized as shown in Scheme 1. The key step in this procedure is the Heck reaction of 2,5-dibromotoluene with two equivalents of 4-(3-propionyloxypropyloxy)styrene to give **1**. Deprotection of the propionyl groups and reaction with acrylic acid under Mitsunobu conditions[12] gave **2**.

The thermal behaviour of **1** and **2** was studied by DSC and polarised optical microscopy. The DSC trace of **1** shows a large melting endotherm ($\Delta H=40$ kJ mol^{-1}) at 116 °C and two smaller transitions at 158 °C ($\Delta H=0.25$ kJ mol^{-1}) and 208 °C ($\Delta H=1.85$ kJ mol^{-1}). Compound **1** recrystallised on cooling and subsequent heating/cooling cycles gave identical results to this first cycle. The propionyl groups of **1** do not undergo thermally induced crosslinking, and hence **1** serves as a useful model compound to study the phase behaviour of more reactive **2**. A birefringent fluid phase between 116 and 208 °C was observed in the polarisation microscope, when compound **1** was heated. At higher temperatures (above 158 °C), the texture could clearly be identified as nematic. However, cooling below the transition at 158 °C, a thin film of **1** sandwiched between two glass slides had a tendency to align homeotropically, and displayed bright flashing when a shear force was applied to the upper glass slide. When filled into a LC testing cell, the LC aligned into a monodomain only when heated above 158 °C; however, the monodomain was retained on subsequent cooling below 158 °C. Also, electrooptical switching[13] with an applied voltage of 9 V could be observed only in the higher temperature phase. These observations suggest the existence of a smectic A phase below the nematic.



Scheme 1 Procedure for synthesis of **1** and **2**.

However, even on extended annealing of uncovered films (3 days), no texture typical of a smectic phase could be formed.

The DSC trace of **2** in the presence of sulfur (3 wt%) as a polymerisation inhibitor also showed three transitions (Fig. 1a): a large melting endotherm at 90 °C (27 kJ mol^{-1}) and two very small transitions at 144 °C (0.1 kJ mol^{-1}) and 210 °C (0.6 kJ mol^{-1}). Polarised optical microscopy of thin films of **2** under ambient conditions revealed that **2** melts into a birefringent fluid at 90 °C and that this birefringence disappeared reversibly at 210 °C. The absence of thermal crosslinking can be assigned to the presence of oxygen, which is known to inhibit acrylate crosslinking.[14,15] The observed optical textures clearly indicate that the transition at 210 °C relates to a nematic–isotropic transition, but the presence of a lower temperature smectic phase below 144 °C cannot be confirmed as extended annealing (several hours) of thin films of **2** at 130 °C in air leads to crosslinking.

Table 1 Thermal properties of **1** and **2**

		Transition temp./°C	Enthalpy/kJ mol^{-1}
Compound **1**	K–S	116	40
	S–N	158	0.25
	N–I	208	1.85
Compound **2**	K–S	90	27
	S–N	144	0.1
	N–I	210	0.6

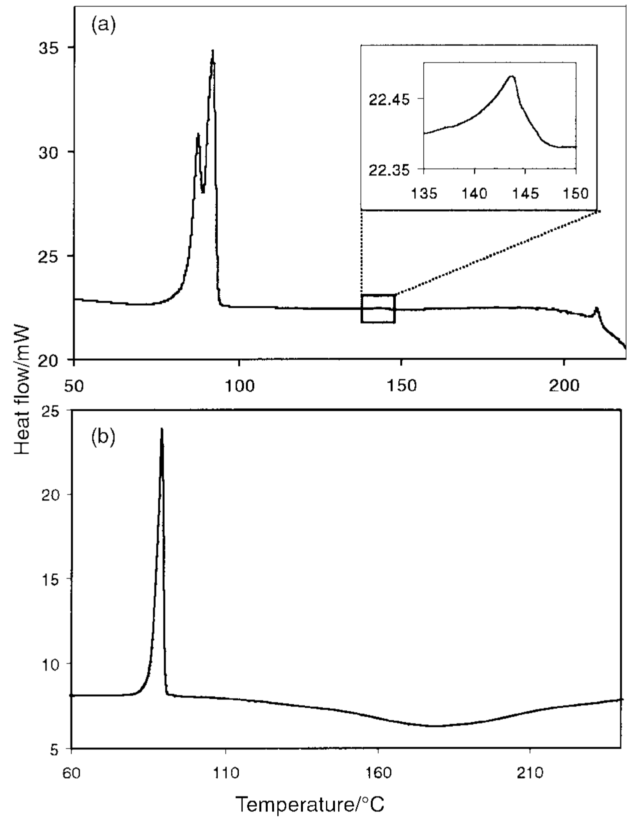


Fig. 1 (a) DSC heating scan (10 °C min^{-1}) of **2** in the presence of 3 wt% sulfur as inhibitor; (b) DSC heating scan (10 °C min^{-1}) of **2** with no added inhibitor.

The interplay between the molecular arrangement of the LC phase and the photophysical properties of **1** has been investigated by measuring the absorption spectra at various temperatures. Fig. 2a shows absorption spectra of **1** recorded in the crystalline state (31 °C), the low temperature LC phase (124 °C), the nematic phase (172 °C) and the isotropic melt (224 °C). The latter absorption spectrum is similar to that obtained in dilute solution (not shown here), where the molecules are isolated from each other and absorb independently. The absorption spectrum of the crystalline state shows the signature of H-aggregation,[16] which typically results from a parallel face-to-face arrangement of neighbouring molecules in a molecular crystal.[17] In this arrangement the single molecule electronic transitions split into a doublet and in the case of a perfect H-aggregate, the low energy transition is strictly forbidden. In the absorption spectrum of **1**, recorded at 31 °C, the high energy transition peaks at 306 nm, and the very weak low energy transition at 406 nm, corresponding to a splitting of 1.00 eV. This figure is in the same order of

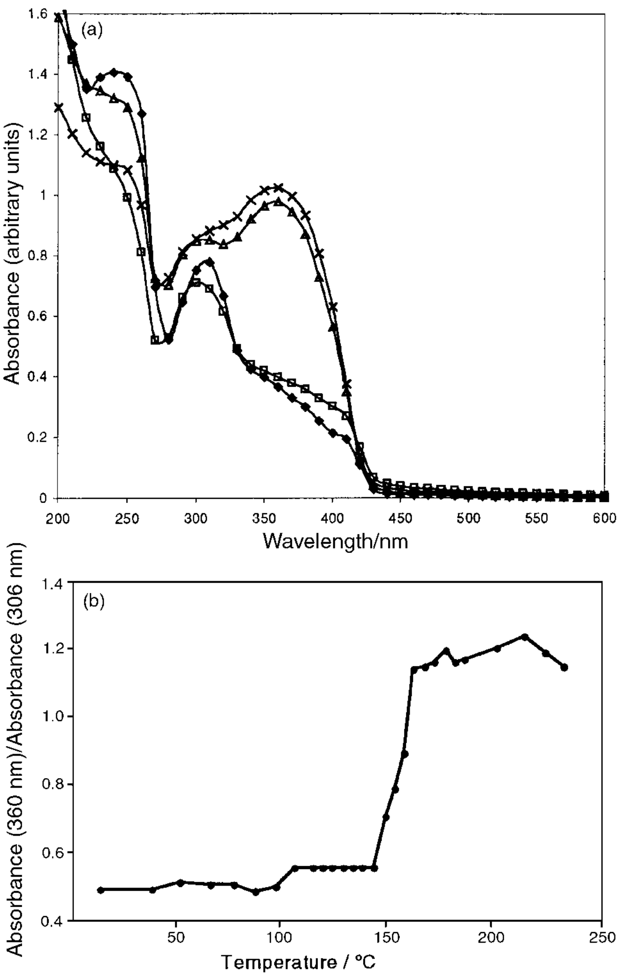


Fig. 2 (a) Absorption spectra of a thin film of **1**, in the crystalline phase (circles; 31 °C), in the smectic phase (squares; 124 °C), in the nematic phase (triangles; 172 °C) and in the melt (crosses; 224 °C); (b) temperature dependence of the ratio of the absorbance at 360 nm to that at 306 nm for compound **1**.

magnitude as reported previously for molecular crystals for thiophene and phenylene oligomers[18] and thiophenevinylene.[19] The absorption spectrum in the lower temperature liquid crystalline phase (Fig. 2a, 124 °C) is almost identical to that of the crystalline phase. It can be concluded that in this phase the molecules also arrange parallel face-to-face, which is consistent with a smectic phase. On transition to the nematic LC phase, Fig. 2a, 172 °C, the spectrum changes dramatically: the previously forbidden absorption rises sharply, resulting in a broader peak which is split only weakly, and much enhanced integral oscillator strength. This indicates the breaking up of molecular stacking on the transition from a smectic to a nematic phase, with the result that H-aggregation is much reduced. The absorption spectrum in the nematic phase is very similar to that of the isotropic phase spectrum. The degree of H-aggregation can be clearly illustrated by plotting the ratio of the absorbance at 360 nm to the absorbance at 306 nm against temperature. The result in Fig. 2b clearly shows a sharp rise of this ratio in the temperature region of the LC–LC transition. On cooling back to room temperature, the shape of the crystalline absorption spectrum is fully recovered, hence it is possible to interpret the spectroscopic results in physicochemical terms, not on the grounds of chemical degradation.

Apart from the textbook case of H-aggregation in conventional molecular crystals,[17–19] previous reports have described H-aggregation in vapour-deposited thin films[20,21] and Langmuir–Blodgett layers.[22] However, to our knowledge there has been no report yet of H-aggregation in a smectic LC, although a number of conjugated smectic LCs have been studied previously, both low molecular weight[23,24] and polymeric.[25]

At room temperature, **2** shows the signature of H-aggregation similar to that of the model compound **1**, with a splitting of 0.95 eV. However, as the experimental setup employed an evacuated sample chamber, a temperature dependent characterisation of the reactive mesogen **2** was not possible. At this stage, we can only speculate that a similar H-aggregated liquid crystalline phase also exists for compound **2**.

Such a phase would be of potential use for EL applications, if it could be transferred into the network *via* crosslinking. In the space charge limited regime of organic devices, the current through a device is limited by carrier mobility, and it is well known that carrier mobilities in molecular materials can critically depend on phase morphology.[23,24,26] For conjugated calamitic LCs, it has been shown that hole[23] as well as electron[24] mobilities can be enhanced by several orders of magnitude on the transition from a nematic to a smectic phase even without H-aggregation. Mobilities may be enhanced further by H-aggregation as face-to-face stacking at short intermolecular distances indicates a favourable molecular arrangement for fast transport. H-aggregates themselves do not emit light,[16,17] however, a small number of molecules not engaged in aggregates (*e.g.*, dopant molecules) can be sufficient for bright emission.

When compound **2** is heated in a DSC without added inhibitor (Fig. 1b) a broad exothermic peak is observed which can be assigned to acrylate crosslinking. The peak onset occurs almost immediately after the melting transition, but the maximum heat flow is found at much higher temperature, at approximately 180 °C. Cooling and reheating gave flat, featureless thermograms indicating complete crosslinking on the first heating scan. To investigate the thermal crosslinking of **2** further, spincoated films were heated to 175 °C at a rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$ under a nitrogen atmosphere. The UV–Vis absorption spectra of the resulting film before and after rinsing and dipping in THF are unchanged (Fig. 3) which indicates that **2** has crosslinked into an insoluble network. Note that the absorption spectrum after thermal treatment shows strongly reduced H-aggregation. The result may be different for photochemical crosslinking which is carried out isothermally at a defined temperature. Photoinitiated acrylate crosslinking is the common curing method for conventional RMs,[17] however, this method will leave residual inhibitor and photoinitiator in the resulting network, which may act as quenching sites for luminescence. Crosslinked networks of **2** show photoluminescence (Fig. 3) when optically excited (360 nm). From the intercept of absorption and PL spectra, the optical gap was estimated as 2.94 eV.

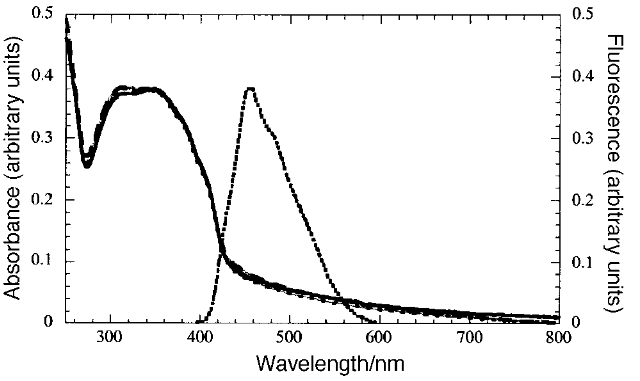


Fig. 3 Absorption spectra of a thin film of **2**: after polymerisation (solid line); after polymerisation and rinsing (short dashes); after polymerisation and dipping (long dashes) and photoluminescence (PL) spectra (dotted line) for a thin film of thermally crosslinked **2**. PL was excited at 360 nm and the intensity was normalised to match the peak height of absorbance. The spectra intersect at 423 nm.

Table 2 The dependence of the dichroic ratio on heating rate

Heating rate/°C $\min^{-1}$	Dichroic ratio
0.1	1.08
0.3	1.57
1	1.74
3	1.53
5	2.03
10	1.36

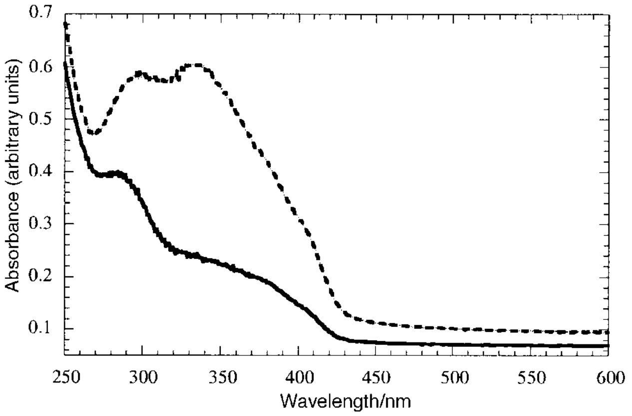


Fig. 4 Dichroic absorption spectra of an aligned, crosslinked film of **2**. Dashed line is the absorbance parallel to alignment direction. Solid line is the absorbance perpendicular to the alignment direction.

Anisotropic networks of **2** can be produced by spin coating concentrated solutions on a substrate coated with a liquid crystal alignment layer. These films were placed under a nitrogen atmosphere and the temperature raised to 175 °C at various heating rates. Polarised absorption spectroscopy showed enhanced absorbance for incident light polarised parallel to the rubbing direction of the alignment layer. Apparently compound **2** melts into the LC phase and aligns into a monodomain, this alignment is partially retained on thermal crosslinking. The dichroic ratios D obtained for the different heating rates are given in Table 2. The highest dichroism ($D \approx 2$) was found for a heating rate of 5 °C $\min^{-1}$. The dichroic ratio may be further enhanced by annealing a film of **2** in the nematic phase prior to crosslinking. This was achieved by heating the film to 170 °C followed by cooling to 130 °C under an ambient atmosphere. Polymerisation was then triggered by purging the sample chamber with nitrogen and increasing the temperature. The resulting dichroic ratos were higher than those achieved with a single heating ramp ($D \approx 3.5$, see Fig. 4), and were less dependent on the heating rate.

Conclusions

We have demonstrated the first steps in a novel approach to polarised EL based on the use of a conjugated reactive mesogen as the photoactive layer. The conjugated reactive mesogen **2** and a model compound **1** have been synthesized and fully characterised. These compounds exhibit two liquid crystalline phases, of which the higher temperature phase can be assigned as nematic, and the lower temperature phase has been tentatively assigned as smectic. In the crystalline phase, **1** and **2** show H-aggregation with pronounced exciton splitting. In the case of the model compound **1**, we have found this aggregation to persist in the lower temperature LC phase, which we tentatively assign as smectic A. Thermal crosslinking of thin films of **2** deposited on an LC alignment layer leads to the formation of anisotropic networks without H-aggregates. These films show PL emission and dichroic ratios for polarised absorption of up to 3.5 have been achieved.

Acknowledgements

The authors wish to acknowledge the EPSRC (GR/M08011), the Royal Society, Merck UK Ltd and Sharp Laboratories of Europe Ltd for their financial support. We also thank David Dunmur, Simon Greenfield, David Coates and Peter Raynes for their helpful suggestions.

References

1 D. D. C. Bradley, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 789; J. Salbeck, *Ber. Bunsenges. Phys. Chem.*, 1996, **100**, 1666; A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 402; H. Sixl, H. Schenk and N. Yu, *Phys. Bl.*, 1998, **54**, 225; A. Greiner, *Polym. Adv. Technol.*, 1998, **9**, 371; R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, L. L. Brédas, M. Löglund and W. R. Salaneck, *Nature*, 1999, **397**, 121.
2 M. Grell and D. D. C. Bradley, *Adv. Mater.*, 1999, **11**, 895.
3 G. Lüssem, F. Geffarth, A. Greiner, W. Heitz, M. Hopmeier, M. Oberski, C. Unterlechner, J. H. Wendorff, *Liq. Cryst.*, 1996, **21**, 903.
4 M. Grell, D. D. C. Bradley, M. Inbasekaran and E. P. Woo, *Adv. Mater.*, 1997, **9**, 798.
5 M. Grell, M. Redecker, K. S. Whitehead, D. D. C. Bradley, M. Inbasekaran and E. P. Woo, *Liq. Cryst.*, 1999, **26**, 1403.
6 M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf and A. Yasuda, *Adv. Mater.*, 1999, **11**, 671.
7 D. J. Broer, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A, Mol. Cryst. Liq. Cryst.*, 1995, **261**, 513.
8 D. J. Broer, J. Lub and G. N. Mol, *Nature*, 1995, **378**, 467.
9 A. P. Davey, R. G. Howard and W. J. Blau, *J. Mater. Chem.*, 1997, **7**, 417.
10 C. W. Tang and S. A. van Slyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
11 R. Schenk, H. Gregorius, K. Meerholz, J. Heinze and K. Müllen, *J. Am. Chem. Soc.*, 1991, **113**, 2634; J. Heinze, J. Mortensen, K. Müllen and R. Schenk, *Chem. Commun.*, 1987, 701.
12 O. Mitsunobu, *Synthesis*, 1981, 1.
13 V. Freedericksz and V. Zolina, *Trans. Faraday Soc.*, 1933, **29**, 919.
14 H. G. Elias, in *Makromoleküle*, 5th edn., Vol. 1, pp. 451, Hüthig-Wipf, 1990, Basel (ISBN 3-85739-101-4).
15 F. R. Wright and G. W. Hicks, *Polym. Eng. Sci.*, 1978, **18**, 378.
16 M. Kasha, H. R. Rawls and M. A. El-Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371.
17 J. D. Wright, *Molecular Crystals*, 2nd edn., pp. 102, Cambridge University Press (ISBN 0-521-47730-1).
18 D. Oelkrug, H. Egelhaaf, J. Giershner and A. Tompert, *Synth. Met.*, 1996, **76**, 249; B. Servet, G. Horowitz, S. Ries, O. Lagorsse, P. Alnot, A. Yasser, F. Deloffre, P. Srivastava, R. Hajlaoui, P. Lang and F. Garnier, *Chem. Mater.*, 1994, **6**, 1809.
19 S. J. Martin, A. J. Cadby, P. A. Lane and D. D. C. Bradley, *Synth. Met.*, 1999, **101**, 665.
20 T. Imamura, K. Watanabe, Y. Tsuboi, H. Miyasaka and A. Itaya, *Thin Solid Films*, 1999, **338**, 243.
21 A. Itaya, T. Imamura, M. Hamaguchi, Y. Tsuboi, H. Miyasaka, T. Asahi and H. Masuhara, *Thin Solid Films*, 1997, **311**, 277.
22 Y. C. Tian, *Langmuir*, 1997, **8**, 1354.
23 M. Funahashi and J. I. Hanna, *Phys. Rev. Lett.*, 1997, **78**, 2184.
24 H. Tokuhisa, M. Era and T. Tsutsui, *Appl. Phys. Lett.*, 1998, **72**, 2639.
25 G. Lüssem, E. Festag, A. Greiner, C. Schmidt, C. Unterlechner, W. Heitz, J. H. Wendorff, M. Hopmeier and J. Feldmann, *Adv. Mater.*, 1995, **7**, 923.
26 D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Nature*, 1994, **371**, 141.

Paper 9/06371D