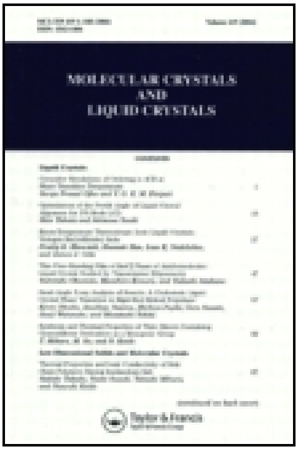

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Electroluminescent Nematic Polymer Networks with Polarised Emission

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Electroluminescent Nematic Polymer Networks with Polarised Emission

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Electroluminescence with a polarisation ratio of 12:1 from a uniformly aligned nematic network is reported. Diene photo-active end-groups were used, which polymerise by a selective cyclisation reaction. Surface alignment was achieved for the first time using a doped polymer photoalignment layer, oriented by exposure to polarised UV light. Threshold voltages between 2 V and 8 V were found and a brightness of 90 cd m^{-2} was obtained. Both the PL and EL intensities were higher after photochemical crosslinking.

Keywords: organic electroluminescence; polarised EL; networks

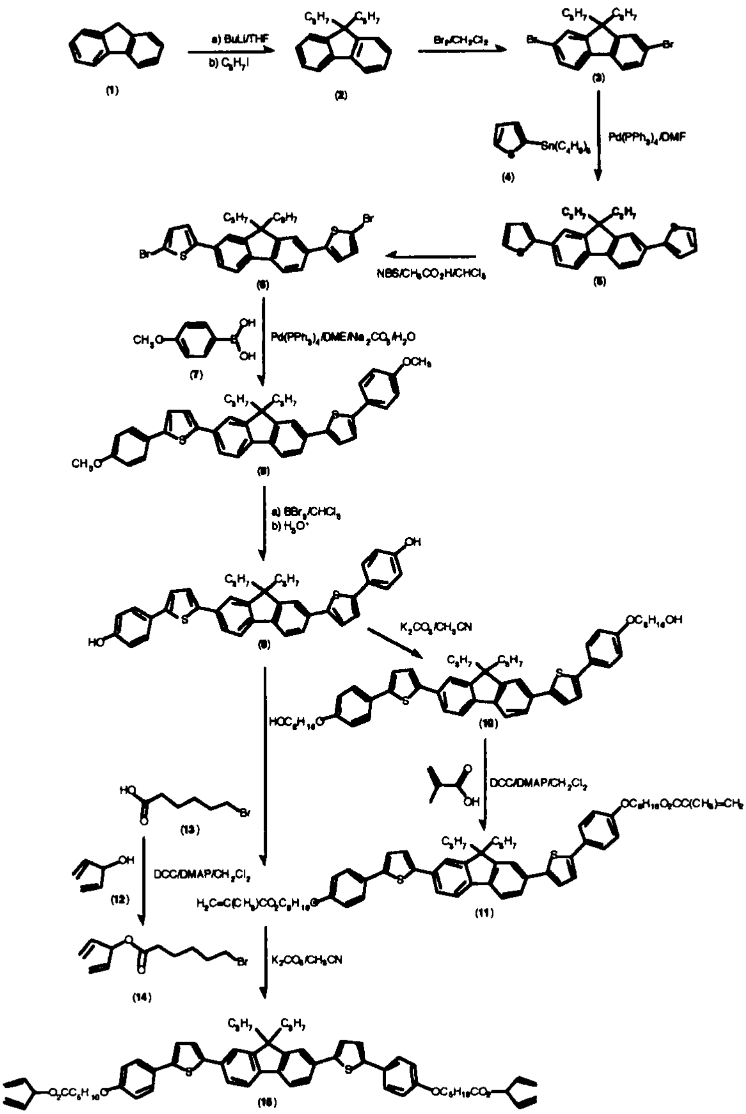
INTRODUCTION

The development of organic light-emitting diodes (OLEDs)[1-3] now offers the prospect of a low cost lighting source with polarised electroluminescence for portable LCDs with a lower power consumption and/or a higher brightness. [2] This can be achieved by replacing one of the polarisers and the back light by a polarised EL light source. EL ratios of 10 or more are adequate with the use of a clean up polariser. Polarised EL can achieved from uniaxially aligned linear chromophores. Best results to date have been obtained using conjugated mainchain polymers.[2,3] An EL polarisation ratio of 12:1 with a brightness of 200 cd m^{-2} was found from *para*-phenylene vinylene rubbed at high temperatures when partially-formed from its soluble polymer precursor.[4] A higher ratio of 15:1, but with lower brightness, was achieved using liquid crystalline polyfluorene films oriented on rubbed polyimide alignment layer.[5] However, in addition to problems associated with mechanical buffing, these high molecular weight polymers are highly viscous. This leads to long annealing times at high temperatures. The conversion of macroscopically oriented reactive mesogens (liquid crystals) to an intractable network provides an alternative route to polarised EL. This technique involves the polymerisation and crosslinking of reactive liquid crystalline monomers *via* photopolymerisable and/or thermally polymerisable end-groups of the molecule. Low temperature processing is possible and multilayer OLED devices can be constructed with carrier-transporting layers deposited on top of the insoluble crosslinked network. Despite these advantages there has been limited success to date using this approach. Polarised EL with a dichroic ratio of 2 was achieved only by doping a liquid crystal network with a photoactive perylene dye.[6] Other authors quote polarised absorbance and PL.[7,8] EL was not reported. Other less practical methods for the macroscopic alignment of EL chromophores have also been reported[9-14].

We now report polarised EL from a stable nematic network formed by photopolymerisation of a liquid crystalline chomophore with diene photopolymerisable endgroups for selective crosslinking attached to the EL by flexible aliphatic spacers. Macroscopic orientation of the chromophore is achieved for the first time by photoalignment techniques using a composite photoalignment/hole transport layer.

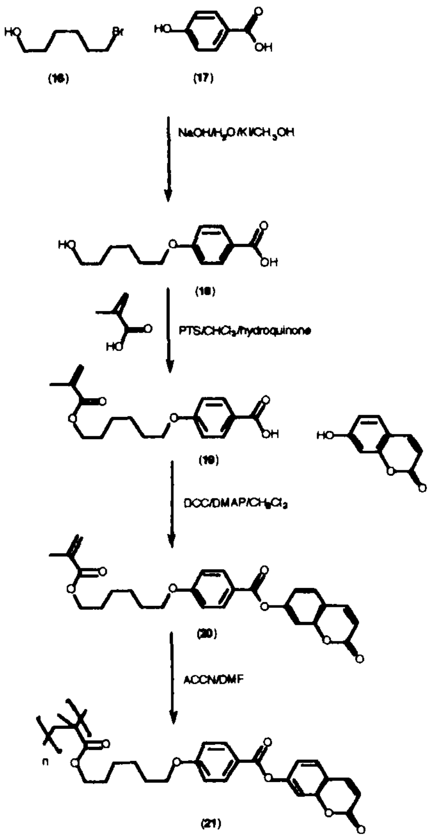
SYNTHESIS

The photopolymerisable liquid crystalline acrylate **11** and the corresponding mesomorphic diene **15** were synthesised as shown in scheme 1. Commercially available fluorene **1** is alkylated in a two-step reaction *via* deprotonation at the 9 position with butyl lithium followed by addition of propyl iodide. This process is carried out twice to generate 9,9-dipropylfluorene **2**. This is then brominated directly using bromine to yield 2,7-dibromo-9,9-dipropylfluorene **3**. A Stille aryl-aryl coupling reaction of **3** with commercially available tributylstanylthiophene **4** yielded the symmetrical dithiophene **5**. Bromination of **5** with *N*-bromosuccinimide in dichloromethane gave the corresponding 2,5-disubstituted thiophene **6**. A palladium catalysed Suzuki aryl-aryl coupling with 4-methoxyphenylboronic acid **7** and the dibromide **6** produced the diether **8**, which was demethylated using boron tribromide in the usual fashion to yield the symmetrical bis-phenol **9**. Alkylation with 8-bromooctanol gave the diol **10**, which was esterified at both ends of the molecule with methacrylic acid chloride and triethylamine in dichloromethane to yield the desired diacrylate **11**. The commercially available 1,4-pentadien-3-ol **12** was esterified with 6-bromohexanoic acid **13** using DCC/DMAP to give the bromo-ester **14**. A Williamson ether alkylation of the bis-phenol **9** with the bromide **14** yielded the desired diene ester **15**.


(1)
a) BuLi/THF
b) C3H7I
C3H7
(2)
Br2/CH2Cl2
Br
(3)
Sn(C4H9)3
(4)
Pd(PPh3)4/DMF
(5)
NBS/CH3CO2H/CHCl3
S
(6)
CH3O
OH
B
(7)
Pd(PPh3)4/DME/Na2CO3/H2O
OCH3
(8)
a) BBr3/CHCl3
b) H3O+
HO
OH
(9)
K2CO3/CH3CN
OC6H12OH
HOC6H12O
(10)
DCC/DMAP/CH2Cl2
OC6H12O2CC(CH3)=CH2
H2C=C(CH3)CO2C6H12O
(11)
HO
O
Br
(13)
OH
(12)
DCC/DMAP/CH2Cl2
(14)
K2CO3/CH3CN
O2CC5H10O
OC5H10CO2
(15)

Scheme 1

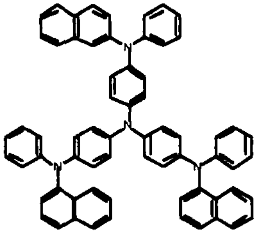
The photoreactive polymer **21** was synthesised as shown in reaction scheme 2. Commercially available 4-hydroxybenzoic acid was alkylated in a Willianson ether synthesis with 6-bromohexanol **16** to yield the 4-(6-hydroxyhexyloxy)benzoic acid **18**, which was esterified with methacrylic acid to yield the methacrylate **19**. Esterification of **19** with commercially available 7-hydroxycoumarin (umbelliferone) with DCC and DMAP gave the monomer **20**. This was polymerised radically to yield the photoreactive sidechain polymer **21**.



Scheme 2

RESULTS AND DISCUSSION

Multi-layer OLEDs were constructed using an indium tin oxide (ITO) coated glass substrate (12 x 12 x 1 mm). The ITO is coated with two strips (~2 mm) of polyimide along opposite edges of the substrate, then covered with a polyethylene dioxythiophene/polystyrene sulphonate (PEDT/PSS), EL-grade, layer of thickness 45 nm ± 10 %. The polymer blend of the photoalignment polymer **21** containing 30% of the hole-injecting, 4,4',4''-*tris*[*N*-(1-naphthyl)-*N*-phenyl-amino]triphenylamine **22** is deposited by spin coating to form a layer of thickness ~20 nm.



(22)

This polymer blend is now photochemically crosslinked through a (2+2) cycloaddition of adjacent coumarin side-chains.[15-18] to form a hole-injecting/aligning network after exposure to linearly polarised UV from an Argon Ion laser tuned to 300 nm. The alignment quality reaches a maximum for a critical fluence and then deteriorates at higher fluences. This is due to competing interactions between the nematic phase and the surface giving rise to either parallel or perpendicular alignment.[16-18] The polarisation ratio of emitted light is not severely affected up to dopant concentrations of 30%, although higher fluences are required to obtain optimum alignment. The liquid-crystalline luminescent layers of either **11** (T_g = 10°C; Cr-N = 68°C; N-I = 120°C) or **15** (T_g = 45°C; Cr-N = 93°C; N-I = 107°C) is then spun cast onto this hybrid hole-transporting/alignment crosslinked network to form a film of ~40 nm thickness after drying. The sample is heated to 100°C and slowly cooled at 0.2°C/min to room temperature to achieve macroscopic alignment of chromophores in the nematic state for **11** or nematic glass phase for **15**. Irradiation with unpolarised UV light at 300 nm induces cross-linking of the photo-active end-groups of either **11** or **15** to form an insoluble and intractable layer. Aluminium electrodes are vapour-deposited under a vacuum of 10^{-6} mbar and silver paste dots applied for electrical contact. The diene **15** polymerises *via* a sterically-controlled, intermolecular cyclisation reaction to form a cyclic polymer product. It yields an intractable, thermally stable network, which is insoluble and allows the addition of other layers, such as electron-transporting compounds.[15-18]

The polymerisation reaction of the diene **15** is slower, but much more selective, than the polymerisation of the analogous methacrylate **11**.

The PL polarisation ratio ($PL_{||}/PL_{\perp}$) of the overlying liquid crystal **15** in its nematic glass phase before crosslinking can be taken as a measure of the alignment quality. Figure 1 shows a polarisation ratio of 11:1 for the diene **15** on the hybrid hole-transport/alignment layer. $PL_{||}/PL_{\perp} > 0$ indicates that the liquid crystal director aligns parallel to the polarisation direction of the incident UV beam. Devices made with **15** in the nematic glassy state showed poor EL polarisation ratios, because the low glass transition temperature compromised the alignment stability. Much better performance was achieved when **15** was crosslinked. The polarisation ratio $EL_{||}:EL_{\perp}$ is 11:1 at the spectral peak. We obtained a brightness of 100 cd m^{-2} (measured without polariser) at a drive voltage of 11 V with an external efficiency of 1.4%. The PL and EL intensities of the crosslinked layer are higher than those of the uncrosslinked diene, see Figure 2 (a) for the PL intensity before and after crosslinking. The threshold and operating voltages are also lower.

The methacrylate **11** polymerises at least 30 times faster than the diene **15**. However, crosslinked layers of the methacrylate **11** show much greater photochemical damage (bleaching) than corresponding layers of the crosslinked diene **15** despite much shorter exposure times, see Figure 2 (b) for the PL intensity before and after crosslinking.

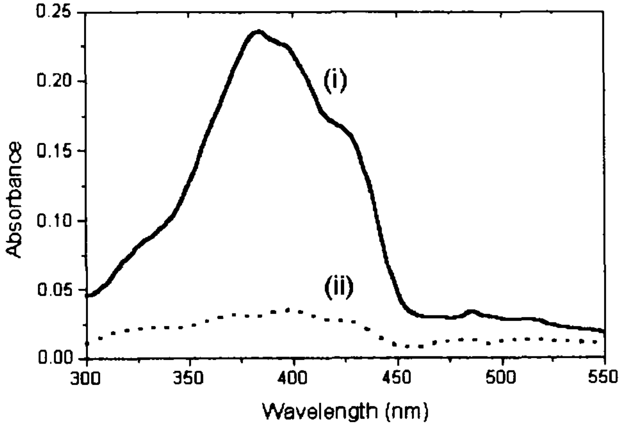


Figure 1. The polarised photoluminescence spectrum [(i) $EL_{||}$ and (ii) $EL_{\perp}$] of the unreacted diene **15** before photochemical crosslinking.

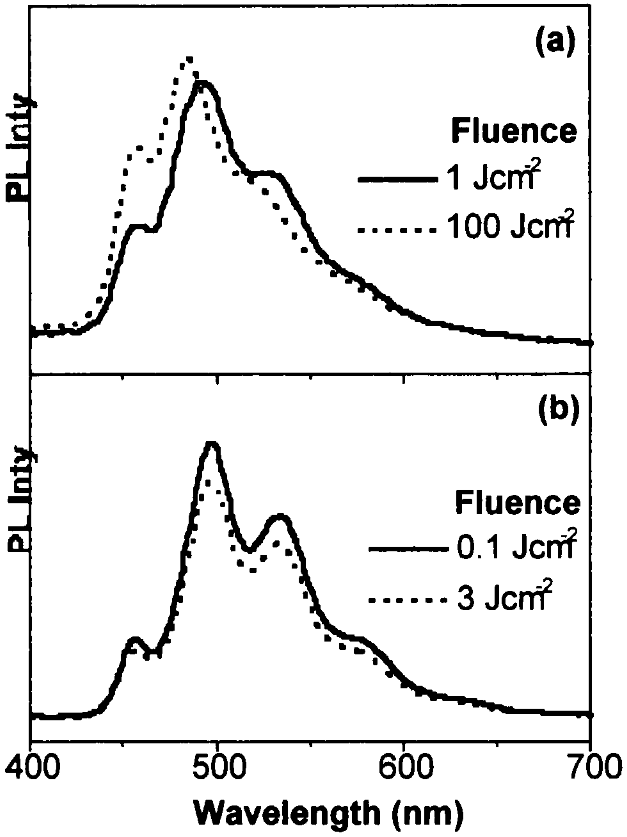


Figure 2. (a) The photoluminescent intensity of the unreacted diene **15** (dashed line) and the corresponding values for the crosslinked polymer network (solid line). (b) The photoluminescent intensity of the unreacted methacrylate **11** (dashed line) and the corresponding values for the crosslinked polymer network (solid line).

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CONCLUSIONS

Electroluminescence with a polarisation ratio of 12:1 and 100 cdm^{-2} at 11 V has been obtained from a crosslinked nematic network. PL and EL intensities are higher after crosslinking than before. Operating voltages are lower. This is probably due to the rigid nature of the alicyclic polymer backbone. Very little photodegradation is observed using dienes as opposed to acrylates. A combined photoalignment/hole transport layer was used to align the EL LC before photochemical crosslinking.

References

[1] C. H. Chen, J. Shi and C. W. Tang, *Macromol, Symp.*, **125**, 1 (1997).
[2] M. Grell and D. D. C. Bradley, *Adv. Mater.*, **11**, 895 (1999).
[3] D. D. C. Bradley, *Curr. Opin. Solid State Mater. Sci.*, **1**, 789 (1996).
[4] M. Jandke, P. Strohriegl, J. Gmeiner, W. Brütting and M. Schwoerer, *Adv. Mater.*, **11**, 1518 (1999).
[5] M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. Nothofer, U. Scherf and A. Yasuda, *Adv. Mater.*, **11**, 671 (1999).
[6] R. A. M. Hikmet, D. B. Braun, A. G. J. Staring, H. F. M. Schoo and J. Lub, *Int. Pat. Appl.* WO 97/07654 (1995).
[7] A. Bacher et al *J. Mat. Chem.*, **9**, 2985 (1999).
[8] A. P. Davey, R. G. Howard and W. J. Blau, *J. Mater. Chem.*, **7**, 417 (1997).
[9] P. Dyreklev, M. Berggren, O. Inganäs, M. R. Anderson, O. Wennerström and T. Hjertberg, *Adv, Mater.*, **7**, 43 (1995).
[10] U. Lemmer, D. Vacar, D. Moses, A. J. Heeger, T. Ohnishi and T. Noguchi, *Appl, Phys. Lett.*, **68**, 21 (1996).
[11] K. Pichler, R. H. Friend, P. L. Burn and A. B. Holmes, *Synth, Metals*, **55–57**, 454 (1993).
[12] V. Cimrová, M. Remmers, D. Neher and G. Wegner, *Adv. Mater.*, **8**, 146 (1996).
[13] T. W. Hagler, K. Pakbaz, K. F. Voss and A. J. Heeger, *Phys. Rev. B*, **44**, 8652 (1991).
[14] N. A. J. M. van Aerle, M. Barmentlo and R. W. J. Hollering, J. *Appl. Phys.*, **74**, 3111 (1993).
[15] M. Schadt, H. Seiberle and A. Schuster, *Nature*, **351**, 212 (1996).
[16] M. O'Neill and S. M. Kelly, *J. Phys., D. Appl. Phys.*, **33**, R67 (2000).
[17] K. Ichimura, *Chem. Rev.*, **100**, 1847 (2000).
[18] A. E. A. Contoret, S. R. Farrar, P. O. Jackson, L. May, M. O'Neill, J. E. Nicholls, S. M. Kelly and G. J. Richards, *Adv. Mater.*, **12**, 971 (2000).