Linearly polarised organic light-emitting diodes (OLEDs): synthesis and characterisation of a novel hole-transporting photoalignment copolymer[†]

Matthew P. Aldred,^{*a*} Panos Vlachos,^{*†*} Adam E. A. Contoret,^{*b*} Simon R. Farrar,^{*b*} W. Chung-Tsoi,^{*b*} Bassam Mansoor,^{*b*} Kai L. Woon,^{*b*} Robert Hudson,^{*a*} Stephen M. Kelly^{**a*} and Mary O'Neill^{**b*}

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We describe the synthesis and characterisation of a novel hole transporting photoalignment copolymer for linearly polarised emission. The copolymer has a coumarin side-chain which undergoes (2 + 2) cycloaddition on irradiation with ultraviolet light. A fluorene side-chain, whose ionisation potential is well matched to the work-function of indium tin oxide, provides hole transporting properties. Polarised green electroluminescence was obtained by spin coating a novel polymerisable and light-emitting liquid crystal onto the photoaligned copolymer. A polarisation ratio value of 13 : 1 and a polarised irradiance of 200 cd m⁻² was obtained at 9 V. Polarised red emission is also described in a guest–host configuration. The spatial patterning of the polarisation direction is also shown.

Introduction

Polarised electroluminescence has several potential uses in electro-optic applications. A major application is to provide a backlight for liquid crystal displays in order to increase their low contrast and brightness by eliminating one of the polarisers and also to reduce their size, weight and power consumption by replacing the lamp. Organic light-emitting diodes (OLEDs) with polarised emission have a range of additional applications; they give better legibility in bright sunlight and the spatial patterning of the polarisation direction of emission can form the basis of a 3-dimensional display.^{1–3}

The first reported OLED with polarised emission utilised a macroscopically aligned film of poly(3-(4-octylphenyl)-2,2'bithiophene) (PTOPT) oriented on a substrate surface of polyethylene.⁴ However, a low polarisation ratio of 2.4 was obtained. Much more efficient polarised EL was exhibited by aligned liquid crystalline, main-chain polymers incorporating a rigid polymer backbone of conjugated aromatic rings, especially poly(9,9-dioctylfluorene).⁵ Efficient polarised emission was also achieved more recently using the corresponding conjugated oligomers with a lower molecular weight.^{6,7} The rigid-rod polymers or oligomers are first aligned in the liquid crystalline state using a mechanically-rubbed surface, such as PPV,^{1,8} doped-polyimide^{1,5} or PEDOT,^{6,7} as the alignment layer and then quenched into the glassy state. The formation of a liquid crystalline glass freezes in the macroscopic alignment of the aromatic main-chain polymer backbone or rigid-rod oligomer and consequently also the orientation of the electroluminescent chromophores incorporated within them. Due to the intrinsically high order parameter of the liquid crystal director obtained using these materials on rubbed alignment surfaces, polarisation ratios achieved using main chain polymers are high (>25: 1). However, the high viscosity of main chain conjugated polymers means that long annealing times at high temperatures are required in order to achieve the desired alignment. Even higher polarisation ratios (up to 33:1) have been obtained using related liquid crystalline fluorene oligomers on rubbed PEDOT.^{6,7} This may be attributable to the lower viscosity of the oligomers compared to that of the analogous polymers, which facilitates a higher degree of molecular reorientation within the liquid crystalline state. However, annealing times at high temperatures of over one hour are still required.

The thin layers present in OLEDs, compared to those in LCDs, means mechanical rubbing can cause substrate and electrode damage, as well as generating dust and static that can act as traps or even lead to device breakdown. Therefore, the use of non-contact photoalignment layers to align the EL chromophores in the LC state appears much more attractive from a commercial production point of view. Photoalignment also offers the important added potential of photolithographic pixel patterning.^{2,3} Photoalignment of electroluminescent materials was first reported using a photopolymerisable nematic liquid crystal, a so-called reactive mesogen (RM), which was subsequently photopolymerised to form an insoluble EL film as a crosslinked polymer network.9 Photoalignment has also been applied to liquid crystalline polyfluorenes more recently using photoaddressable polymers (PAPs).¹⁰ The PAPs used for the polyfluorene alignment are methacrylate comb polymers containing mesogenic and non-mesogenic azobenzene side-chains. Liquid crystalline PAPs were obtained by increasing the concentration of mesogenic side-chains. Good alignment was only observed using the LC PAPs. EL

^aDepartment of Chemistry, University of Hull, Hull, UK HU6 7RX. E-mail: s.m.kelly@hull.ac.uk; Fax: +44 01482 466410; Tel: +44 01482 465464

^bDepartment of Physics, University of Hull, Hull, UK HU6 7RX. E-mail: m.oneill@hull.ac.uk; Fax: +44 01482 465606;

Tel: +44 01482 465501

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[‡] ZLX Techno Ltd, 3 Trinity Lane, Beverley, UK HU17 0DY.

polarisation ratios of 14 at a brightness of up to 200 cd m⁻² and efficiency of 0.3 cd A⁻¹ were demonstrated. Improved efficiencies (0.66 cd A⁻¹) have been achieved using ultrathin PAP layers (5 nm, compared to 20 nm previously).¹¹ A mainchain photoalignment hole-transporting polymer was reported recently.¹² However, the LC alignment was poor and polarised EL was not demonstrated.

The alignment of *small* molecules, rather than that of oligomers or polymers, in the nematic phase appears to be a more attractive approach, as spontaneous alignment can be achieved, i.e., the long thermal annealing process used to induce alignment of oligomers and polymers is not required. This approach also requires the stabilisation of the macroscopic alignment induced either by formation of the "glassy state" or fixation by photochemical crosslinking. For example, even though polarised EL was obtained at 70 °C in the smectic X phase from a low-molecular-mass liquid crystalline 2-(4-hexyloxyphenyl)-5-(4-hexyloxybiphenyl-4'-yl)oxadiazole (HOBP-OXD) on rubbed polyimide,¹³ a low polarisation order parameter (0.32), poor brightness (0.8 cd m^{-2}) and low quantum efficiency (2.8×10^{-5}) were observed. This material crystallises at lower temperatures. In contrast, the alignment of a photocrosslinkable glass-forming nematic liquid crystal by photoalignment on a coumarin photoalignment layer occurs at room temperature.9 A polarised emission ratio of 11 : 1 and brightness of 60 cd m^{-2} were obtained. Photoalignment of small molecules in the nematic state is clearly an attractive approach to fabricating OLEDs with polarised emission. Unfortunately, due to the nonconducting nature of the coumarin photoalignment material, doping with a charge-transporting triarylamine was necessary.9 However, triarylamines are non-planar and relatively high concentrations (50%) of the hole-transport dopant led to a reduction in the alignment quality of the liquid crystalline glass. Phase separation at high dopant concentrations is also a potential problem. Therefore, the synthesis of hybrid holetransporting photoalignment layers with rod-like or lath-like shape would appear to be a promising technological approach to address these problems. Therefore, in this paper we report the synthesis and characterisation of a novel conducting photoalignment polymer with rod-like hole-transport sidechains. We also demonstrate the alignment of a novel lightemitting and photopolymerisable liquid crystal and the subsequent generation of linearly polarised electroluminescence from the corresponding crosslinked polymer network.

Design considerations

Coumarin side-chain polymers have been extensively used as photoalignment materials for nematic LCs for liquid crystal displays. On irradiation with linearly polarised light, the probability of a photochemical reaction is proportional to $\cos^2\phi$ where ϕ is the azimuthal angle between the polarisation direction **P** of the incident beam and the transition dipole moment of the coumarin side-chain. As first shown by Schadt *et al.*,¹⁴ the coumarin side-chains are depleted anisotropically by a 2 + 2 cycloaddition as illustrated in Fig. 1 for a model side-chain polymer with a coumarin group at the end of the side-chain attached to a polymethacrylate backbone. The

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COUMARIN MODEL MONOMER COUMARIN MODEL DIMER



Fig. 1 2 + 2 Cycloaddition for a model coumarin molecule. *P* indicates the polarisation direction of the incident ultraviolet beam.

nematic liquid crystal is subsequently deposited and aligns homogeneously with its director oriented parallel and perpendicular to **P** for weak and strong polarised UV illumination respectively.^{15,16} Spectroscopic analysis shows that the competition between two independent LC-surface interactions determines the resultant director orientation.¹⁶ Parallel LC alignment is determined by a short-range steric interaction with the dimerised cyclobutane side-chains. The LC alignment direction switches from parallel to perpendicular above a critical fluence and subsequently the LC alignment is determined by a dispersive LC interaction with the intact sidechains in the bulk of the photoalignment layer. The alignment direction of luminescent reactive mesogens remains parallel to the polarisation direction of the UV beam onto the photoalignment layer irrespective of its fluence.9 This implies that alignment is governed by the short-range interaction of the LC with the dimerised coumarin photoproduct rather than with the unreacted coumarin.

We propose a coumarin based copolymer to provide both hole-transporting and photoalignment properties. The ionisation potential of the material should be well matched to that of the indium tin oxide (ITO) anode (\approx 4.8 eV) to minimise the energy barrier for injection of holes. The film should provide planar and uniaxial planar liquid crystal alignment without and following polarised UV irradiation respectively. The coumarin groups must be relatively mobile so that they can easily orient into the conformation required for dimerisation. Hence main-chain copolymers incorporating the holetransporting and coumarin units were not considered because of their high viscosity. A side-chain copolymer is more likely to give efficient crosslinking, since the coumarin and holetransporting side-chains can be attached via flexible aliphatic spacers to a polymethacrylate backbone. Another design consideration is that 2 + 2 cycloaddition is only possible between closely spaced neighbours so that a high fraction of coumarin side-chains is required. This affects hole transport, which involves a series of intermolecular hops of charge carriers between the hole-transporting side-chains. The hopping probability depends on the overlap of the wave-functions of the aromatic molecular cores and so has an inverse exponential dependence on the core separation. We use a linear hole-transporting moiety to reduce the intermolecular hopping distances and to minimise disruption with the

photoalignment process. Indeed, the low fraction of holetransporting side-chains may be an advantage for our class of light-emitting liquid crystals, whose injection and transporting properties are much better for holes than for electrons. The photoalignment copolymer reduces the hole-current and so improves the balance of positive and negative charge in the device improving its efficiency.

Synthesis

Monomer 1 was synthesised as shown in Scheme 1. First a Stille coupling¹⁷ of 2-(tributylstannyl)thiophene and 1-bromo-4-octyloxybenzene 1 afforded the thiophene 2, see Scheme 1. The tributylstannyl derivative 3 was synthesised by reaction of compound 2 with *n*-BuLi in THF at -78 °C followed by the addition of tri-n-butyltin chloride.¹⁸ The tributylstannyl derivative 3 was found to be sensitive to acidic conditions and undergo destannylation on contact with silica gel.¹⁹ Fortunately the crude product was pure enough to be used

(iv)

C₃H₇ C₃H₇

CaH7 CaH

10

C₃H₇ C₃H

(v

(vi) C3H7 C3H7

12

(vii)

Sn(C₄H₉);

(C₄H₉)₃Si

OC₈H₁₇

Scheme 1 Reagents and conditions: (i) 2-(tributylstannyl)thiophene, $Pd(PPh_{3})_{4}$, DMF, 90 °C, (ii) a) *n*-BuLi, THF, -78 °C, b) Sn(C₄H₉)₃Cl, (iii) C₆H₁₃MgBr, PdCl₂(dppf), diethyl ether, reflux, (iv) tributylammonium bromide, 50% NaOH(aq), 1-bromopropane, toluene, reflux, (v) Pd(PPh₃)₄, DMF, 90 °C, (vi) a) BBr₃, CH₂Cl₂, 0 °C, b) H₂O (ice), (vii) a) K₂CO₃, butanone, reflux, b) 2,6-di-tert-butyl-4methylphenol (BHT), RBr.

monomer 1

in the next step. 1,4-Dibromobenzene 4 was monoalkylated by reaction with the Grignard reagent formed from hexylbromide and magnesium,²⁰ to produce 1-bromo-4-hexylbenzene (5). A Stille coupling¹⁷ of 2-(tributylstannyl)thiophene and the aryl bromide 5 afforded the thiophene 6, which was converted to the corresponding tributylstannyl derivative 7 in the usual way.¹⁸ The asymmetrical di-alkylated fluorene 9 was synthesised in a one step alkylation procedure from commercially available 2-bromo-7-iodofluorene 8.²¹ Selective reaction at the iodo-group of the fluorene 9 with the octyloxy-substituted tributylstannyl derivative 3²² in a Stille aryl-aryl coupling reaction gave the aryl bromide 10. A second Stille reaction at the bromo-group of the fluorene 10 using the hexyl-substituted tributylstannyl derivative 7 vielded the asymmetrical 2,7disubstituted fluorene 11. Removal of the octyloxy-chain of the ether 11 using boron tribromide afforded the asymmetrical phenol 12, which was alkylated using 6-bromohexyl methacrylate derivative, in a Williamson ether reaction, to afford monomer 1.

Monomer 2 was synthesised according to a modified pathway shown in Scheme 2.14,16 Williamson-ether reaction of the commercially available p-hydroxybenzoic acid methylester 13 with commercially available 1-bromohexanol afforded the ester 14, which was saponified to produce the carboxylic acid 15.²³ Esterification of the hydroxyl group of compound 15 using methacroyl chloride produced the polymerisable benzoic acid derivative 16,²⁴ which was esterified with 7-hydroxycoumarin 17 using DCC and DMAP to produce the coumarin

Copolymerisation of monomer 1 and monomer 2 was carried out by a thermally induced radical polymerisation, using

Scheme 2 Reagents and conditions: (i) 1-bromohexanol, K₂CO₃, butanone, (ii) a) KOH, EtOH, H₂O, b) H₃O⁺, (iii) methacryloyl chloride, DMA, BHT, dioxane, 60 °C, (iv) DCC, DMAP, BHT, CH₂Cl₂, room temperature.

C₃H₇ C₃H





co-polymer, X:Y = 1 : 4, $T_g = 69 \,^{\circ}C$

Scheme 3 Reagents and conditions: (i) AIBN, THF.

AIBN as initiator, see Scheme $3.^{25}$ to produce **copolymer 1** (x = 1; y = 4). The ¹H NMR showed no presence of the two olefinic hydrogens at $\delta_{\rm H}$ 5.55/5.56 and $\delta_{\rm H}$ 6.11, confirming that no monomer was present in **copolymer 1**. The chemical structures of the light-emitting reactive mesogens **RM 1** and **RM 2** used to generate polarised electroluminescence are shown in Fig. 2.

Results and discussion

We first show that 2 + 2 cycloaddition occurs on irradiation of **copolymer 1** with ultraviolet light from a HeCd laser at 325 nm. Fig. 3 shows the absorbance spectrum of a thin film before and after irradiation using a fluence of 10 J cm⁻². By comparison with the absorption spectra of the monomers, the peaks at 224 nm and 276 nm can be unambiguously assigned to the coumarin side-chain. The intensity of both these peaks is reduced on irradiation with ultraviolet light indicating 2 + 2 cycloaddition.¹⁶ The weaker and broader peak at 400 nm is assigned to the fluorene side-chain. The absorbance spectrum above 350 nm is magnified by a factor of 4 in Fig. 3 to show that the absorbance of the fluorene side-chain is unaffected by irradiation.



Fig. 3 Absorption spectrum of **copolymer 1** before and after irradiation with ultraviolet light of wavelength 325 nm and fluence 10 J cm⁻². The spectral region above 350 nm is magnified for clarity (\times 4).



Fig. 4 Cyclic voltammogram of **copolymer 1**. The potential, *E*, is measured with respect to that of the saturated calomel electrode.

The ionisation potentials (IP) of the compounds were measured electrochemically by cyclic voltammetry using a computer-controlled scanning potentiostat (Solartron 1285). The cyclic voltammetry scan for **copolymer 1** is shown in Fig. 4. The potential, *E*, is plotted with respect to that of the saturated calomel electrode. The onset potential for oxidation, E_{ox} is clearly defined by a step change in current and is obtained from the intersection of the two tangents at the current discontinuity. IP is obtained using the empirical relationship proposed by Bredas *et al.*: IP = $[E_{ox} + 4.4] \text{ eV.}^{26}$ Copolymer 1



Fig. 2 Structures of the green light-emitting reactive mesogen RM 1 (upper; Cr–N = 52 °C; N–I = 143 °C; $T_g = 0$ °C) and red light-emitting reactive mesogen RM 2 (lower; Cr–N = 142 °C; N–I = 123 °C; $T_g < 15$ °C).

has an IP value of 5 eV, which is well matched to the workfunction of an ITO/PEDOT anode for the injection of holes. The oxidation process is electrochemically and chemically reversible showing that **copolymer 1** is stable to oxidation and as such it is suitable as a hole injection material. The IP of the light-emitting **RM 1** is also found to be 5.0 eV so that there is no barrier for injection of holes from the copolymer. The hole mobility of **copolymer 1** was too dispersive for measurement. However, the hole mobility of a series of reactive mesogens containing the same aromatic core as **monomer 1** varies from 2×10^{-5} cm² V⁻¹ s⁻¹ to 1×10^{-3} cm² V⁻¹ s⁻¹ depending on the chromophore separation. As discussed above, we expect the hole mobility of **copolymer 1** to be even lower because of the low fraction of the hole-transporting component so that a thin layer was used in polarised EL devices.

Having shown that the photoalignment copolymer 1 exhibits (2+2) cycloaddition and hole-injecting properties, we use it to produce a polarised OLED. The photoalignment and lightemitting organic layers were sandwiched between a PEDOT hole injection layer on ITO coated glass and a commercially available hole-blocking layer (TAZ). A LiF/Al cathode was used for electron injection. A thin film of the green RM 1 was deposited by spin-casting onto a thin film of copolymer 1, which was previously irradiated with polarised UV light. The liquid crystal RM 1 retains a metastable supercooled nematic phase at room temperature on heating above the melting point and subsequent cooling. Hence, uniform alignment of the chromophore was obtained by annealing the sample at 110 °C and slowly cooling to room temperature. The alignment direction of the chromophore was parallel to the polarisation direction of the UV beam. The subsequent room temperature photopolymerisation of **RM 1** gives a thermally stable and robust polymer network without any loss of alignment. The photopolymerisation process is discussed in more detail elsewhere.^{16,22} Fig. 5 shows the polarised electroluminescence spectrum from the device. A peak polarisation intensity ratio EL_{para}/EL_{perp}, where para (perp) refer to light parallel (perpendicular) to the alignment direction, of 13 : 1 is obtained. The polarisation ratio is maximum for the zero phonon EL peak indicating that it is slightly reduced by vibronic coupling. Typical current-voltage and luminancevoltage plots are shown as electronic supplementary information (ESI).[†] The device has a luminance of 300 cd m^{-2} at 10 V and a maximum efficiency of 1.6 cd A^{-1} . This is an improvement on previous data for a polarised OLED using photoalignment.¹¹ The low threshold voltage, 4.2 V at 2 cd m⁻², and the insertion of copolymer 1 between the anode and lightemitting layer of the OLED confirm that the photoalignment polymer is an effective hole transporting material. The alignment direction of copolymer 1 was spatially patterned by exposing adjacent squares with orthogonally polarised light. Photoluminescence (PL) from RM 1 deposited on top appears uniform except when viewed through a polariser. Then the orthogonally aligned areas appear green and black when the polarisation direction of the polariser is parallel to the director of one of these regions.²⁷ A movie, deposited as electronic supplementary information (ESI),† shows changes in the PL image as the polariser is rotated.

Photoalignment can also be used to align electroluminescent materials in a guest-host configuration. The red-emitting RM 2 crystallises rather than retaining a supercooled nematic phase on cooling to room temperature. Hence, polarised red PL was obtained by energy transfer in a guest-host blend prepared by doping the red guest RM 2 in the green host RM 1 with a ratio of 1:3 by weight. The absorbance spectrum of RM 2 overlaps the PL spectrum of RM 1 so that efficient Förster energy transfer is possible. Fig. 6 shows polarised PL from a film of the guest-host combination aligned using the photoaligned copolymer 1. The emission is red with no residual green component from RM 1. The polarisation ratio, PL_{para}/PL_{perp}, is wavelength dependent as indicated in Fig. 6. The maximum value of 7 : 1 is smaller than that obtained for a red-emitting oligomer reported recently, probably because of the lower order parameter of compound RM 2.²⁷



Fig. 5 Polarised electroluminescence (EL) spectrum from an OLED. The solid and dashed lines show the EL spectrum of the photochemically crosslinked green **RM 1** on a thin crosslinked film of the photoaligned **copolymer 1** parallel and perpendicular to the alignment direction. The dots show the wavelength dependence of the EL polarisation intensity ratio, EL_{para}/EL_{perp} , where para (perp) refer to light parallel (perpendicular) to the alignment direction.



Fig. 6 The solid line shows the parallel component of the photoluminescence (PL) from a photochemically crosslinked guest host mixture of **RM 2** : **RM 1** in ratio 1 : 3 by weight on a thin crosslinked film of the photoaligned **copolymer 1**. The dots show the wavelength dependence of the PL polarisation intensity ratio, PL_{para}/PL_{perp} , where para (perp) refer to light parallel (perpendicular) to the alignment direction.

Conclusions

A hole-transporting/coumarin photoalignment **copolymer** has been synthesised that consists of **monomer 1** (rod-like hole-transporting material) and **monomer 2** (coumarin-photoalignment material) in a 1 : 4 ratio. Only a small proportion of the hole-transporting material was incorporated into the copolymer to preserve the alignment properties of the coumarin moiety. The green chromophore **RM 1** was aligned on this hybrid hole-transporting photoalignment layer for the production of linearly polarised light, in which a peak polarisation intensity ratio of 13 : 1 and polarised electroluminescent irradiance of 200 cd m⁻² was obtained at 9 V. Optimisation of this new class of patternable hole-transporting/coumarin photoalignment polymer will almost certainly lead to much higher values for the polarisation ratio.

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