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Synthesis of UV-curable liquid crystalline diacrylates for the application of polarized electroluminescence

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Two series of UV-curable rod-like diacrylates containing bis-tolane (M1–M5) and bis-stilbene (M6–M10) mesogens were synthesized. All of the diacrylates were prepared through convergent syntheses involving palladium-catalysed coupling reactions. The thermal transitions and mesomorphic properties of the diacrylates were characterized by differential scanning calorimetry and optical microscopy. All the bis-tolane-based monomers reveal nematic phases, except M5 which shows no mesomorphic behaviour. For the bis-stilbene based monomers, most show no mesomorphic behavior and only M7 and M9 exhibit a SmA phase.

1. Introduction

Oriented liquid crystal (LC) networks, an interesting class of polymeric materials, are highly promising for a diverse range of applications. Optical anisotropy is an important property of oriented liquid crystalline networks. This kind of optically anisotropic LC network can be used as an optical compensation film for a liquid crystal display (LCD) to resolve its narrow viewing angle problem [1]. Oriented LC networks can be obtained by photopolymerization of difunctional LC monomers in contact with unidirectionally rubbed thin film substrates. During polymerization, the ordering of the mesogen is fixed, yielding a uniaxially crosslinked network [2]. Since the first report of polarized electroluminescence (EL) utilizing an organic semiconductor by Dyreklev et al., [3] a number of approaches have been reported to realize polarized EL devices [4-20].

In general, polarized EL can be achieved from uniaxially aligned chromophores, and this combination of organic EL with well established LCD technology offers the possibility of low cost, bright, portable displays with the combined benefits of simplified manufacture and enhanced power efficiency. As an optional approach to polarized EL, UV-curable mesogens were first reported by O'Neill, Kelly and coworkers [11]. The key conceptual advantage of the UV-curable system is based on the solubility properties of reactive LC monomers; whereas the conversion of macroscopically oriented reactive monomers to an intractable network provides an alternative route to

In this study, we report the syntheses and characterization of UV-curable LCs that combine liquid crystallinity, reactive end groups and fluorescence in each monomer, as well as the application of a nematic M1 network on the polarized EL device.

2. Experimental

2.1. Materials and methods

All reagents and solvents used in the synthesis were purchased from Aldrich and ACROS Chemical Co. and used directly without further purification. NMR spectra with TMS as internal standard were recorded on a Varian VXR-300 spectrometer (300 MHZ) and chemical shifts are reported in units of ppm. Thermal transitions and thermodynamic parameters were determined by a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) equipped with a liquid nitrogen

polarized EL. Reactive LC monomers are small molecules before crosslinking, and have a number of advantages over polymers. They are soluble in more organic solvents, and typically melt at low temperatures into lower viscosity liquid crystals that offer easier monodomain alignment. After crosslinking, however, UV-curable LCs form an insoluble network. This technique involves the polymerization and crosslinking of reactive liquid crystal monomers via photo and/or thermally polymerizable end groups of the molecule. Hence, UV-curable LCs lend themselves readily as active layers in advanced multilayer device architectures, that not only make low temperature processing possible, but also facilitate sub-pixellation by selective photopatterning [14].

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cooling accessory. Heating and cooling scanning rates were 10°C min⁻¹ with calibration against indium as standard. Mesophase identifications were achieved with a Carl–Zeiss Axiphot polarizing optical microscope (POM) equipped with a Mettler FP 82 hot stage and a FP 90 central processor. Fourier transform infrared (FTIR) spectra were measured on a Perkin Elmer Spectrum One FTIR Spectrometer, using KBr pellets.

2.2. Synthesis

Two types of conjugated calamitic reactive mesogens (RMs), a bis-tolane series (M1–M5) [21] and a bis-stilbene series (M6–M10), were surveyed as model compounds for the studies. The syntheses of the investigated compounds were carried out following the pathways shown in schemes 1 and 2. The acrylate moieties are known as the most common photopolymerizable group used in LC networks, partly because of the high chemical reactivity of the radicals produced after the initiation step. The synthetic route to acrylate bis-tolane homologues (M1–M5) involved the coupling of a diiodobenzene and 6-(4-ethynylphenoxy)hexan-1-ol derivative intermediates followed by esterification with acryloyl chloride, as depicted in scheme 1. The acrylate

THF,
$$Et_3N$$

R1

 R_2
 R_3
 R_2
 R_1
 R_2
 R_3
 R_3
 R_4
 R_4
 R_5
 R_5

Scheme 1. Synthesis of bis-tolane monomers M1–M5.

M4: R1=CH(CH₃)₂, R2=C₂H₅, R3=H

M5: R1=C₂H₅, R2=OCH₃, R3=OCH₃

Scheme 2. Synthesis of bis-stilbene monomers M6-M10.

bis-stilbene series (M6–M10) was derived from the contribution of a series of aromatic core units (a–e) coupling with isoeugenol (2) derivatives, followed by esterification, as outlined in scheme 2. The materials were fully characterized by NMR, IR and MS, with results consistent with the proposed structures. The purities of M1–M10, which were checked with HPLC, were higher than 99.5%.

2.2.1. 1,4-Bis{[4-(6-hydroxyhexan-1-yloxy)phenyl]ethynyl}-2-ethylbenzene (1a). 1-[4-(6-Hydroxyhexan-1-yloxy)phenyl]acetylene (7.62 g, 35.20 mmol), bistriphenylposphine)palladium(II) chloride (0.20 g, 0.28 mmol), copper(I) iodide (0.27 g, 1.50 mmol), triphenylphosphine (0.73 g, 2.70 mmol) and 1,4-diiodo-2-ethylbenzene (5.00 g, 14.10 mmol) were dissolved in 50.0 ml of triethylamine under an atmosphere of nitrogen. The mixture was heated at 80°C for 24 h. The solvent was removed by rotory evaporator and the crude product was dissolved in ethyl acetate. The ethyl acetate solution was extracted with ammonium chloride and then washed with water, saturated NaCl solution and

dried over anhydrous MgSO₄. After evaporating the ethyl acetate, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane 1/1), yield 3.36 g (67%) of a yellow compound, m.p.=105.1°C. ¹H NMR (CDCl₃, δ ppm): 1.29–1.34 (t, 3H, Ph–CH₂–C $\underline{\text{H}}_3$), 1.38–1.86 (m, 16H, Ph–O–CH₂–(C $\underline{\text{H}}_2$)₄–), 2.84–2.92 (q, 2H, Ph–C $\underline{\text{H}}_2$ –CH₃), 3.64–3.74 (t, 4H, HO–C $\underline{\text{H}}_2$ –), 3.95–4.03 (t, 4H, Ph–O–C $\underline{\text{H}}_2$ –), 6.84–7.45 (m, 11H, aromatic protons). ¹³C NMR (CDCl₃, δ ppm): 13.8, 23.1, 25.5, 26.0, 29.2, 32.6, 56.4, 62.8, 67.7, 84.0, 95.5, 110.7, 113.3, 114.6, 115.5, 130.6, 132.1, 137.0, 153.6, 157.1.

2.2.2. 1,4-Bis{[4-(6-acrloyloxyhexan-1-yloxy)phenyl] ethynyl}-2-ethylbenzene (M1). 1,4-Bis{[4-(6-hydroxyhexan-1-yloxy)phenyllethynyl}-2-ethylbenzene 2.55 mmol) was dissolved in a mixture of dry THF (30.00 ml) and triethylamine (1.50 ml, 10.00 mmol) under an atmosphere of nitrogen. After cooling the solution in an ice-water bath to 0°C, acryloyl chloride (0.51 g, 5.10 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The solid formed was taken into ethyl acetate and the solution washed with water. The organic layer was dried with MgSO₄. After filtration, the solvent was removed by rotary evaporation and the residue purified by column chromatography (silica gel, ethyl acetate/hexane 1/4), yield 1.46 g (78%) of a yellow compound; purity 99.6%. ¹H NMR (CDCl₃, δ ppm): 1.27–1.33 (t, 3H, Ph–CH₂– CH₃), 1.29–1.47 (m, 8H, Ph–O–CH₂–CH₂–(CH₂)₂– CH₂-), 1.67-1.81 (m, 8H, Ph-O-CH₂-CH₂-(CH₂)₂-CH₂-), 2.85-2.93 (q, 2H, Ph-CH₂-CH₃), 3.95-4.03 (t, 4H, Ph-O-CH₂-), 4.15-4.21 (t, 4H, -COO-CH₂-), 5.79–5.85 (d, 2H, H–CH=CH–COO–), 6.10–6.18 (m, 2H, H-CH=CH-COO-), 6.38-6.44 (d, 2H, H-CH= CH–COO–), 6.84–7.45 (m, 11H, aromatic proton). ¹³C NMR (CDCl₃, δ ppm): 13.8, 23.0, 25.7, 25.8, 28.5, 29.1, 56.4, 64.5, 67.6, 84.0, 95.5, 110.7, 113.3, 114.6, 115.4, 128.5, 130.5, 131.5, 132.7, 132.9, 153.6, 157.1, 166.3. FTIR (KBr, cm⁻¹): 2981, 2940, 2867 (-CH₂-), 2207 $(-C \equiv C-)$, 1723 (C=O), 1636 (C=C), 1603, 1567, 1512 (C-C in Ar), 1283, 1246 (COC). MS (EI, m/z): 646 (M^+) . Elem. anal. cacld for C₄₂H₄₆O₆: C 78.02, H 7.12; found C 78.20, H 7.22%.

2.2.3. 1-(6-Hydroxyhexyloxy)-2-methoxy-4-propenylbenzene (2). 2-Methoxy-4-propenylphenol (6.50 g, 39.60 mmol), 6-chloro-1-hexanol (4.92 g, 36.00 mmol), potassium carbonate (10.93 g, 79.20 mmol) and potassium iodide (0.60 g, 3.60 mmol) were dissolved in 200 ml of acetonitrile under an atmosphere of nitrogen. The mixture was heated at 80°C for 24 h, and excess

potassium carbonate was filtered off. The solvent was evaporated and the crude product was taken into ethyl acetate. The ethyl acetate solution was extracted with 5% hydrochloric acid and the solution washed with water, saturated NaCl solution and dried over anhydrous MgSO₄. After evaporating ethyl acetate, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane 1/1), yield 7.90 g (83%) of a white compound, m.p.=85.8°C. ¹H NMR (CDCl₃, δ ppm): 1.20–1.42 (m, 8H, Ph–O–CH₂–(CH₂)₄–), 2.04 (s, 3H, CH=CH-CH₃), 3.62-3.68 (t, 2H, HO-CH₂-), 3.84 (s, 3H, Ph-O-CH₃), 3.92-4.08 (t, 2H, Ph-O- CH_2 -), 6.00–6.32 (m, 2H, Ph–CH=CH-), 6.70–6.92 (m, 3H, aromatic proton). 13 C NMR (CDCl₃, δ ppm): 18.2, 26.2, 28.8, 32.1, 55.6, 62.2, 68.2, 111.3, 119.4, 126.4, 130.1, 133.2, 148.7, 149.1. FTIR (KBr, cm⁻¹): 3394 (OH), 3020 (-CH=CH-), 2934, 2859 (-CH₂-), 1601, 1581, 1512 (C–C in Ar), 1261, 1227 (COC). MS (EI, m/ z): 264 (M⁺).

2.2.4. 4,4'-Bis(6-hydroxyhexan-1-yloxy)-3,3'-dimethoxy-bis-α-methylstilbene (3a). 1-(6-Hydroxyhexyloxy)-2methoxy-4-propenylbenzene $(2.40 \,\mathrm{g},$ 9.10 mmol), dibromobenzene (0.98 g, 4.13 mol), palladium acetate $(0.02 \,\mathrm{g},$ $0.08 \,\mathrm{mmol}$), tri(o-tolyl)phosphine (0.05 g, 0.17 mmol) and triethylamine were placed in a Pyrex tube under an atmosphere of argon. The solution was heated at 100°C for 36h and then cooled to room temperature. The solid formed was taken into dichloromethane and the solution washed with water, then dried with MgSO₄. After filtration, the solvent was evaporated and the residue purified by column chromatography (silica gel, ethyl acetate/hexane 2/1), yield 1.0 g (40%) of a white compound, m.p. = 72.5° C. ¹H NMR (CDCl₃, δ ppm): 1.26–1.92 (m, 16H, Ph–O– $CH_2-(CH_2)_4-$), 2.24 (s, 6H, $CH=CH-CH_3$), 3.62–3.68 (t, 4H, HO-CH₂-), 3.87 (s, 6H, Ph-O-CH₃), 3.92-4.05 $(t, 4H, Ph-O-CH_2-), 6.82 (s, 2H, Ph-CH=CCH_3-Ph),$ 6.88–7.42 (m, 10H, aromatic proton). ¹³C NMR $(CDCl_3, \delta ppm)$: 17.3, 25.5, 26.3, 28.7, 32.1, 55.7, 62.1, 68.2, 111.5, 111.9, 124.7, 129.6, 131.2, 135.5, 141.6, 144.1, 148.8, 149.0. FTIR (KBr, cm⁻¹): 3333 (OH), 2981, 2935, 2861 (-CH₂-), 1598, 1577, 1513 (C-C in Ar), 1256, 1228 (COC). MS (EI, m/z): 602 (M⁺).

2.2.5. 4,4'-Bis(6-acryloyloxyhexan-1-yloxy)-3,3'-dimethoxy-bis-α-methylstilbene (M6). Compound **3a** (0.40 g, 0.66 mmol) was dissolved in a mixture of dried THF and triethylamine (0.70 ml, 5.31 mmol) under an atmosphere of nitrogen. After cooling the solution in an ice-water bath to 0°C, acryloyl chloride (0.30 ml, 2.66 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and

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stirred overnight. The solid formed was dissolved in ethyl acetate and the solution washed with water, then dried with MgSO₄. After filtration, the solvent was removed by rotary evaporation and the residue purified by column chromatography (silica gel, ethyl acetate/ hexane 1/4), yield 0.40 g (85%) of a white compound, m.p.=62.3°C; purity 99.7%. ¹H NMR (CDCl₃, δ ppm): 1.26-1.90 (m, 16H, Ph-O-CH₂-(CH₂)₄-), 2.24 (s, 6H, $CH=C-CH_3$), 3.87 (s, 6H, Ph-O-CH₃), 3.92-4.05 (t, 4H, Ph-O-CH₂-), 4.13-4.18 (t, 4H, -COO-CH₂-), 5.79-5.82 (d, 2H, H-CH=CH-COO-), 6.10-6.19 (m, 2H, H-CH=CH-COO-), 6.38-6.43 (d, 2H, H-CH=CH-COO-), 6.82 (s, 2H, Ph-CH=CCH₃-Ph), 6.88–7.42 (m, 10H, aromatic proton). ¹³C NMR $(CDCl_3, \delta ppm)$: 17.4, 26.1, 26.3, 28.6, 28.8, 55.7, 62.5, 68.1, 111.5, 112.0, 124.7, 128.7, 129.6, 131.3, 135.2, 141.6, 144.1, 148.8, 148.9, 166.6. FTIR (KBr, cm⁻¹): 2981, 2939, 2862 (-CH₂-), 1722 (C=O), 1636, 1619 (C=C), 1600, 1578, 1512 (C-C in Ar), 1294, 1268, 1245 (COC). MS (EI, m/z): 710 (M⁺). Elem. anal. cacld. for C₄₄H₅₄O₈ C 74.37, H 7.61; found C 74.48, H 7.50%.

2.3. Fabrication and characterization of polarized EL devices

Alignment layers were fabricated by spin-coating poly (ethylenedioxythiophene)poly(styrenesulphonic acid) (PEDOT/PSS) aqueous solution onto ITO glass substrates. After baking, the PEDOT/PSS was rubbed by a rubbing machine and used as the alignment layer. The polymerization mixtures were made by dissolving 99 wt% of the monomer M1 and 1 wt% of benzophenone used as the photoinitiator. The oriented monomers were polymerized with UV of intensity 1.2 J cm⁻² at 350 nm.

The polarized UV-vis spectra were measured by a Shimadzu UV-1601 spectrophotometer with a polarizer

placed between sample and detector. Spectra were obtained with the polarizer aligned parallel or perpendicular to the rubbing direction. Polarized ratios were defined as the parallel to perpendicular intensity. Polarized photoluminescence (PL) measurements were measured by a Shimadzu RF-5301 PC spectrofluorophotometer with a polarizer.

Polarized LEDs were fabricated on ITO-coated glass substrates cleaned sequentially in ultrasonic baths of detergent, deionized water, 2-propanol, deionized water, and acetone. Oxygen plasma treatment was used for 3 min as the final step of cleaning to improve the contact angle just before film forming. Onto the ITO glass an alignment layer (PEDOT/PSS) film was spincoated and rubbed. The monomer solutions (15 mg ml) which were prepared by dissolving the corresponding monomers in toluene, were spin-coated on top of the rubbed PEDOT/PSS surface. After annealing in the liquid crystalline phase, the aligned monomers were cured by illuminating with UV light. Finally, 35 nm calcium and 100 nm aluminum cathodes were deposited onto the aligned emitting films by thermal evaporation through a shadow mask. The polarized device properties were determined by a Photo Research PR-650 Spectra Scan. Spectra were obtained with the polarizer aligned parallel and perpendicular to the rubbing direction.

3. Results and discussion

3.1. Thermal behaviour

Table 1 summarizes the phase transition temperatures and corresponding enthalpy changes of monomers M1–M10. Among the first series of bis-tolane based monomers, M1–M4 exhibit enantiotropic nematic phase. The phase transition temperatures were affected by the lateral substituents. Both M1 and M4 contain a

Table 1. Transition temperatures and corresponding enthalpy changes of monomers M1–M10. Cr=crystal, N=nematic, SmA=smectic A, I=isotropic.

	Phase transition temperatures (°C) and enthalpies (kJ mol ⁻¹)				
Monomers	Heating	Cooling			
M1	Cr 57.2 (36.2) N 93.3 (0.8) I	I 90.8 (−1.1) N<−50°C Cr ^a			
M2	Cr 62.4 (17.6) N 84.6 (2.1) I	I 79.5 (-0.92) N 31.0 (-8.3) Cr			
M3	Cr 29.9 (16.8) N 74.5 (1.32) I	I 69.3 (-1.5) N 17.1 (-16.5) Cr			
M4	Cr 53.0 (34.4) N 71.9 (1.2) I	$I 65.2 (-1.4) N < -50^{\circ} C Cr^{a}$			
M5	Cr 100.3 (28.3) I	I 98.2 (-26.6) Cr			
M6	Cr 62.3 (17.3) I	I 39.6 (-14.3) Cr			
M7	Cr 68.5 (14.1) SmA 86.8 (8.8) I	I 82.6 (-7.3) SmA 63.1 (-12.2) Cr			
M8	Cr 78 (24.2) Í	I 74.8 (-19.8) Cr			
M9	Cr 111.5 (42.4) I	I 81.4 (-12.7) SmA 66.8 (-29.1) Cr			
M10	Cr 85 (28.6) I	I 78.2 (-26.4) Cr			

^aNo crystallization peak was observed even when the sample was cooled below -50°C.

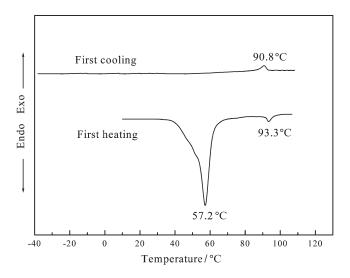
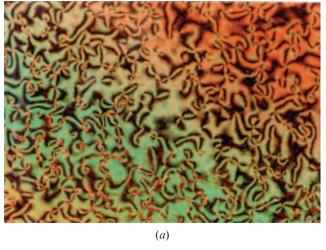


Figure 1. DSC thermogram of monomer M1.

lateral ethyl group (R2) in the middle phenyl ring. The only difference for both compounds was the lateral substituents (R1) in both side phenyl groups. M4, with a bulky isopropyl substituent (R1), shows much lower melting and isotropization temperatures. This is because the lateral isopropyl groups increase the width of the molecule and decrease the packing density of the LC molecules. As a result, the temperatures required to melt the crystals and to clear the LC phase are much lower. Comparing the chemical structures of M2 and M3, the only difference between them was also the lateral substituent (R1) on both side phenyl groups. Again, M3 with the bulky isopropyl group exhibits much lower melting and isotropization temperatures. M5 shows no mesomorphic behaviour, which could be due to the bulky dimethoxy substituents on the middle phenyl ring. Figure 1 shows representative DSC thermograms of monomer M1. The heating scan shows a crystalline to nematic phase transition at 57.2°C and a nematic to isotropic phase transition at 93.3°C. On the cooling scan, an isotropic to nematic exotherm is observed at 90.8°C. No crystallization exotherm is seen even on cooling to -50.0° C. Figure 2(a) shows the typical nematic texture for M1 and figure 2(b) shows the typical smectic A texture for M7. As can be seen from table 1, only two out of the five bis-stilbene derivatives (M6-M10) give liquid crystalline behaviour and specifically a smectic A phase. The other three monomers are not liquid crystalline. This could be due to the symmetry of the structures of monomers M6, M8 and M10.

3.2. Optical study

Aligned samples for further experiments were prepared by annealing the liquid crystalline monomers on a glass



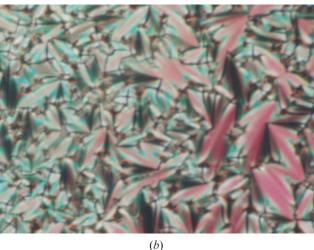


Figure 2. Photomicrographs of (a) the N phase schlieren texture of M1 at 75° C, (b) the SmA phase focal-conic texture of M7 at 75° C.

plate whose surface was coated with PEDOT/PSS. The PEDOT/PSS surface was mechanically rubbed prior to the spin-coating of liquid crystalline monomers on the glass substrate.

The optical properties of aligned liquid crystals were characterized by UV-vis absorption along with PL emission. The results are shown in table 2. The UV absorption peaks of monomers M1–M4 occur at around 340 nm while those of monomers M7 and M9 occur at 362 and 447 nm, respectively. To estimate the degree of alignment achieved, the polarized spectra were recorded with the polarizer placed parallel and perpendicular to the rubbing direction. Figure 3 shows polarized UV and PL spectra of M1. The results indicate that absorbance parallel to the rubbing direction was much higher than that perpendicular to the rubbing direction. This means that the mesogens

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T-1.1.2	TC1	T TX 7 : - : 1. 1 -	- 1	DI		1			. C
i abie 2.	1 ne	U v -visible	absorption.	, PL	emission	ana	polarized	ratio	of monomers.

	1177		Polarized ratio					
Monomer	${ m UV}_{ m max}$ absorption/nm	PL _{max} emission/nm	UV-vis (UV _{//} /UV _{\(\)})	PL ($PL_{//}/PL_{\perp}$)	EL (EL///EL $_{\perp}$)			
M1	343	428	11.7	10.8	7.0			
M2	344	427	12.0	11.1	6.9			
M3	343	429	13.3	11.5	6.8			
M4	340	425	14.0	11.1	6.2			
M7	362	455	4.6	3.5	_			
M9	447	544	4.2	3.4	_			

are aligned parallel to the rubbing direction, and the dichroic ratios calculated from the polarized UV as well as PL spectra for the two types of materials are in the range 3.4–14.0 (table 2); consequently, the dichroic ratios of the nematic monomers are typically higher than those of the smectic monomers. The SmA order parameter is usually higher than the nematic, and this is unfavorable for alignment of monomers on the alignment layer [22].

3.3. Polymer LEDs

To realize further progress in LC polymer network OLEDs, the luminescent material M1 was deposited by spin-coating onto the alignment layer (PEDOT/PSS), forming a nematic phase above 57°C with a clearing point at 93°C. Alignment of a liquid crystalline glass is normally achieved by heating into the isotropic phase, followed by slow cooling for maximum ordering in the aligned nematic phase. Since supercooling occurs in the cooling process, M1 can be crosslinked in the nematic state at ambient temperature by exposure to unpolarized UV radiation to induce polymerization of the reactive acrylate end groups. This yields an intractable, thermally stable LC network, which is insoluble in THF.

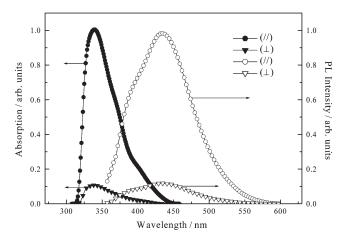


Figure 3. Polarized optical spectra of LC network of M1 on rubbed PEDOT films.

To examine the potential application of these materials, light-emitting devices were constructed with M1 as the active layer with PEDOT/PSS-coated ITO glass as the anode and Ca/Al as the cathode. Figures 4 and 5 show the luminance-voltage and current density-voltage characteristics for the EL device of M1 after

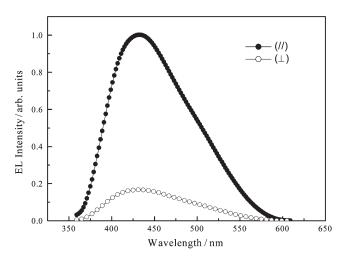


Figure 4. Polarized EL spectra of an ITO/rubbed PEDOT/LC network of M1/A1/Ca device.

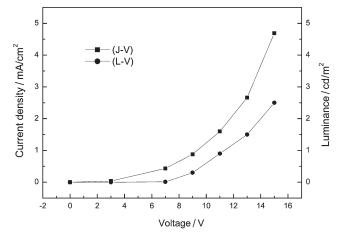


Figure 5. The J-V (\blacksquare) and L-V (\bullet) curves of ITO/rubbed PEDOT/M1/A1/Ca device.

exposure to minimum UV radiation to form an insoluble network. We found that 1.2 J cm⁻² was the minimum UV radiation required to form an insoluble network, which yielded a maximum emission at 450 nm in the blue region with a turn-on voltage for current at 3 V. However, some photodegradation of M1 may occur even with this minimal exposure, although some EL is still obtained from a crosslinked polymethacrylate LC network. The luminance intensity increased with increasing applied voltage, giving a maximum luminance $2.5 \,\mathrm{cd}\,\mathrm{m}^{-2}$. The intensity of the emitted light recorded parallel to the rubbing direction was approximately one order of magnitude greater than that of the perpendicular at the same applied voltage. with regard to these data, the chromophore was aligned predominantly along the rubbing direction where $R_{\rm EL} = EL_{\parallel}/$ EL_{\perp} is a dichroic ratio with EL_{\parallel} and EL_{\perp} being the values of the polarized emission parallel and perpendicular to the rubbing direction. Table 2 gives a comparison of the dichroic ratio calculated from the polarized UV, PL and EL spectra of the materials M1-M4, the values shown are in the range 6.2-8.4. Of course, a maximum luminance 2.5 cd m^{-2} is not acceptable for practical applications and thus these systematic studies have to be optimized.

4. Conclusions

We have synthesized two series of UV-curable rodlike diacrylates containing bis-tolane and bis-stilbene mesogens. The UV-curable monomers show polarized PL and EL properties in the blue region. They can be aligned in the nematic phase by the rubbing method and form an anisotropic polymer network. The liquid crystalline monomers give rise to a wealth of information concerning structure-property relationship in respect of melting points, transition temperatures, mesophase morphologies, optical anisotropy and polarized electroluminescence, with the dichroic ratio of the nematic homologues typically higher than that of the smectic cases. The M1 device yielded a maximum emission at 450 nm in the blue region with a turn-on voltage for current at 3 V. The luminance intensity increased with increasing the applied voltage, with a maximum luminance of 2.5 cd m⁻². Further systematic studies are now necessary to improve the dichroic ratio and to increase the luminance of these systems.

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References

- [1] H. Hasebe, H. Takatsu, Y. Imura, S. Kobayashi. *Jpn. J. Appl. Phys. Part 1*, 33, 6245 (1994).
- [2] C.S. Hsu, H.L. Chen. J. Polym. Sci. A: Polym. Chem., 37, 3929 (1999).
- [3] P. Dyreklev, M. Berggren, O. Inganas, M.R. Andersson, O. Wennerstrom, T. Hjertberg. Adv. Mater., 7, 43 (1995).
- [4] U. Lemmer, D. Vacar, D. Moses, A.J. Heeger, T. Ohnishi, T. Noguchi. *Appl. Phys. Lett.*, 68, 3007 (1996).
- [5] G. Lussem, F. Geffarth, A. Greiner, W. Hitz, M. Hopmeier, M. Oberski, C. Unterlechner, J.H. Wendorff. Liq. Cryst., 21, 903 (1996).
- [6] M. Grell, D.D.C. Bradley, M. Inbasekaran, E.P. Woo. Adv. Mater., 9, 789 (1997).
- [7] M. Grell, D.D.C. Bradley. Adv. Mater., 11, 895 (1999).
- [8] A. Bacher, P.G. Bentley, D.D.C. Bradley, L.K. Douglas, P.A. Glarvey, M. Grell, K.S. Whitehead, M.L. Turner. J. Mater. Chem., 9, 2985 (1999).
- [9] K.S. Whitehead, M. Grell, D.D.C. Bradley, M. Jandke, P. Strohriegl. Appl. Phys. Lett., 76, 2946 (2000).
- [10] K.S. Whitehead, M. Grell, D.D.C. Bradley, M. Inbasekaran, E.P. Woo. Synth. Met., 111–112, 181 (2000).
- [11] A.E.A. Contoret, S.R. Farrar, P.O. Jackson, S.M. Khan, L. May, M. O'Neill, J.E. Nicholls, S.M. Kelly, G.J. Richards. Adv. Mater., 12, 971 (2000).
- [12] M. O'Neil, S.M. Kelly. Adv. Mater., 15, 1135 (2003).
- [13] M.P. Aldred, A.J. Eastwood, S.M. Kelly, P. Vlachos, A.E.A. Contoret, S.R. Farrar, B. Mansoor, M. O'Neill, W.C. Tsoi. *Chem. Mater.*, 16, 4928 (2004).
- [14] M.P. Aldred, A.E.A. Contoret, S.R. Farrar, S.M. Kelly, D. Mathieson, M. O'Neill, W.C. Tsoi, P. Vlachos. Adv. Mater., 17, 1368 (2005).
- [15] M. Grell, W. Kmoll, D. Lupo, A. Meisel, T. Miteva, D. Nether, H.G. Nothofer, U. Scherf, A. Yasuda. Adv. Mater., 11, 671 (1999).
- [16] D. Neher. Macromol. Rapid Commun., 22, 1365 (2001).
- [17] A.C.A. Chen, S.W. Sean, S.W. Culligan, Y. Geng, S.H. Chen, K.P. Klubek, K.M. Vaeth, C.W. Tang. Adv. Mater., 16, 783 (2004).
- [18] Y. Geng, A.C.A. Chen, J.J. Ou, S.H. Chen, K. Klubek, K.M. Vaeth, C.W. Tang. *Chem. Mater.*, 15, 4352 (2003).
- [19] S.W. Culligan, Y. Geng, S.H. Chen, K. Klubek, K.M. Vaeth, C.W. Tang. *Adv. Mater.*, **15**, 1176 (2003).
- [20] S.W. Chang, A.K. Li, C.W. Liao, C.S. Hsu. Jpn. J. Appl. Phys., 41, 1374 (2002).
- [21] C.S. Hsu, K.F. Shyu, Y.Y. Chuang, S.T. Wu. *Liq. Cryst.*, **27**, 283 (2000).
- [22] H. Tokuhisa, M. Era, T. Tsutsui. Appl. Phys. Lett., 72, 2639 (1998).