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Liquid crystalline chromophores for photonic band-edge laser devices

Stephen M. Morris [a,*], Malik M. Qasim [a], Damian J. Gardiner [a], Philip J.W. Hands [a], Flynn Castles [a], Gouli Tu [b], Wilhelm T.S. Huck [b], Richard H. Friend [c], Harry J. Coles [a]

[a] Centre of Molecular Materials for Photonics and Electronics, Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA, UK
[b] Melville Laboratory for Polymer Synthesis, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK
[c] Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, UK

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ABSTRACT

We present results on laser action from liquid crystal compounds whereby one sub-unit of the molecular structure consists of the cyano-substituted chromophore, {phenylene-bis (2-cyanopropene)}, similar to the basic unit of the semiconducting polymer structure poly(cyanoterephthalylidene). These compounds were found to exhibit nematic liquid crystal phases. In addition, by virtue of the liquid crystalline properties, the compounds were found to be highly miscible in wide temperature range commercial nematogen mixtures. When optically excited at $\lambda = 355$ nm, laser emission was observed in the blue/green region of the visible spectrum (480–530 nm) and at larger concentrations by weight than is achievable using conventional laser dyes. Upon increasing the concentration of dye from 2 to 5 wt.% the threshold was found to increase from $E_{th} = 0.42 \pm 0.02$ μJ/pulse ($\approx$20 mJ/cm^2) to $E_{th} = 0.66 \pm 0.03$ μJ/pulse ($\approx$34 mJ/cm^2). Laser emission was also observed at concentrations of 10 wt.% but was less stable than that observed for lower concentrations of the chromophore.

1. Introduction

Research on band-edge laser devices based upon liquid crystals (LCs) has garnered interest in recent years due to the remarkable combination of characteristics that are achievable with this type of organic laser [1–3]. Studies carried out in the literature have shown that LC laser devices are characterized by features such as single-mode emission, wide-band wavelength tunability, and micron-sized resonator structures [1]. Consequently, these compact, wavelength tunable organic laser devices are of significant interest for a wide range of applications including large-area, compact display devices and medical diagnostic techniques.

In general, these lasers typically consist of a chiral LC, which self-organizes to form a helical structure with periodic optical properties, and a fluorescent compound in the form of a laser dye that is dispersed into the host matrix. Previously, the materials that have typically been used as the chromophores in the LC lasers are the π-conjugated small molecules that were developed for conventional liquid 'jet-stream' dye lasers [4]. Typically, these dyes are push–pull chromophores consisting of electron-donating and electron-withdrawing functionalities which, when dispersed into solvents, exhibit high quantum yield and fluorescence lifetimes of the order of a few nanoseconds. Research on LC lasers has demonstrated that these high quantum efficiencies can be retained in chiral LC hosts for dyes such as pyrromethene 597 and, as a result, this can lead to relatively high slope efficiencies of approximately 30% for single-pass device architectures [5] and 60% for LC lasers on silicon backplanes [6]. However, one drawback with these dyes is their miscibility in liquid crystalline media, which is usually limited to about 3 wt.% in the LC host before aggregation of the dye begins to occur.

Recent studies have been carried out on alternative chromophores in the form of pyrene dyes, oligothiophene analogues and oligofluorene structures that have been functionalized with pendant alkyl chains so that they are soluble in a LC host [7–12]. These chromophores typically possess an absorption band at long ultraviolet wavelengths (360–450 nm) with a peak emission wavelength at around 470–500 nm and, due to the preferential alignment with the director, have been shown to exhibit a high order parameter of the transition dipole moment (0.6–0.7) when dispersed into a nematic LC host. Consequently, the laser threshold is lowest at the long-wavelength photonic band-edge, which has been confirmed experimentally [7,8]. All these structures have high quantum yields and this is of importance for low-threshold laser emission. As an example, by comparing the pyrene laser dye with the DCM (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostryl)-4*H*-pyran) laser dye, it was shown that the pyrene-based LC laser had a substantially lower threshold [12].

Additional benefits of the oligofluorene dyes have also been reported [8–11]. Specifically, a study has shown that an oligofluorene dye dispersed into a commercially available chiral nematogen

* Corresponding author.
E-mail address: smm56@cam.ac.uk (S.M. Morris).

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mixture can lead to improved temporal and spatial stability of the LC laser output when compared with the laser dye DCM, although the excitation threshold and slope efficiency were found to be the same for both dyes for the so-called single transverse mode [8]. A further study demonstrated that, using oligofluorene structures, it is possible to combine fluorescence with an intrinsic chirality which, depending upon the handedness, can assist in forming the helical structure. Many of the oligofluorene compounds that were studied did not exhibit any liquid crystalline behaviour and were limited to low concentrations. There were found to be some exceptions namely that the polyfluorene polymer and the oligofluorene compounds containing chiral centres did show liquid crystalline behaviour at high temperatures ($T > 150\,°C$) [10,11]. Oligofluorene structures are also particularly effective for use in LC lasers based upon cholesteric glasses where it was demonstrated that the laser output of the glass film was stable with time at high input powers unlike a conventional fluid LC laser consisting of the same dye and concentration thereof [9].

A poly-phenylenevinylene derivative with triptycene groups has also been considered for LC lasers [18,19]. In this case, the addition of the triptycene groups prevented strong interpolymer interactions, which generally limits the solubility and the efficiency. The results showed that low thresholds were observed as a result of a high order parameter of the transition dipole moment in the liquid crystalline host. The polyfluorenes and the poly-phenylenevinylene have also received considerable attention from the point of view of semiconducting polymer devices, for which they were first developed [13–17]. As a result, it is well known that such structures exhibit high gain and laser action either in blends or when confined to high Q-factor micro-cavities.

Nevertheless, despite their high quantum yields, both the oligofluorene compounds and the poly-phenylenevinylene derivatives are not readily miscible with low-molar mass liquid crystals up to large concentrations. Therefore, the motivation for this study was to develop new compounds that combine liquid crystalline properties with the photoluminescence of the chromophores from the semiconducting polymers so as to ensure a greater compatibility with low molar mass materials. Towards this end, we have synthesized liquid crystalline nematogens that consist of the phenylene-bis (2-cyanopropene) chromophore, which is the repeating unit of the cyano-substituted poly(*p*-phenylenevinylene) polymer. These compounds are found to exhibit enantiotropic nematic LC phases as well as broadband photoluminescence when optically excited at wavelengths between 355 nm and 450 nm. Moreover, when combined with a wide temperature range chiral nematic host these compounds exhibit laser emission up to large concentrations by weight (10 wt.%). Because of the inherent liquid crystallinity of the chromophore, this approach enables a higher concentration of the dye to be dispersed into the LC host than is achievable with the small conjugated organic molecules that are used as laser dyes. Herein, the photoluminescence properties of the structures are discussed and laser emission is observed under optical excitation.

2. Synthesis and characterization

Three different compounds based upon the phenylene-bis (2-cyanopropene) chromophore were synthesised each one exhibiting a nematic liquid crystalline phase. The synthetic route was as follows: 2,4′-Difluorobiphenyl-4-ol (1 eq.) was condensed with 1,9-dibromononane (1 eq.) in the presence of acetone and potassium carbonate. The reaction mixture was refluxed for 3 days and was monitored by thin layer chromatography. After the completion of the reaction, the mixture was extracted with dichloromethane (DCM) three times. The organic layers were separated and evaporated to dryness under reduced pressure. The resultant product was chromatographed (silica gel, DCM:hexane, 1:1) and the desired product [1-bromo-9-(2′,4-difuorobiphenyl-4′-yloxy)nonane] was obtained as a major fraction in good yield (63%). This was followed by a reaction with an equimolar amount of 4-hydroxybezaldehayde in the presence of acetone and potassium carbonate, refluxed for 2 days. At the completion of the reaction, the mixture was extracted with DCM (3×100 mL) and organic layers were separated and evaporated to dryness. The resultant product was isolated through column chromatography (silica gel, DCM:hexane, 2:1). The major fraction was collected as a desired product *p*-[1-(2′,4-difuorobiphenyl-4′-yloxy)-9-nonyloxy]bezaldehayde (**a**), (81%). This compound was further condensed with 1,4-phenylenediacetonitrile and 4-hexyloxybenzaldehyde in equimolar quantities in the presence of potassium *tert.*butoxide (0.1 eq) and ethanol. The resultant mixture was refluxed under nitrogen atmosphere for 10 h. At the completion of the reaction, the solvent was removed under reduced pressure and chromatographed (silica gel, DCM:hexane, 1:1) to obtain desired products (**b,c, and d**) as three separate fractions.

2.1. Compound *b*

Yield (18%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97–7.83 (m, 4H, ArH), 7.69 (s, 4H, ArH), 7.49 (s, 2H, CH), 7.00–6.93 (m, 4H, ArH), 1.84–1.76 (m, 4H, OCH_2), 1.51–1.44 (m, 4H, CH_2), 1.39–1.32 (m, 8H, CH_2), and 0.96–0.89 (m, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.43 142.31(CH), 135.18, 131.52, 126.29, 126.17, 118.45 (CN), 115.05 (ArC), 107.42 (C), 68.40, 31.69, 29.23, 25.80, 22.73 (CH_2), and 14.17 (CH_3).

2.2. Compound *c*

Yield (19%), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.9, 1.9 Hz, 4H, ArH), 7.71 (s, 4H, ArH), 7.51 (s, 2H, CH), 7.46 (ddd, J = 8.9, 5.4, 1.9 Hz, 2H, ArH), 7.29 (t, J = 8.9 Hz, 1H, ArH), 7.10 (t, J = 8.7 Hz, 2H, ArH), 6.98 (dd, J = 8.9, 1.9 Hz, 4H, ArH), 6.75 (dd, J = 8.9, 1.9 Hz, 1H, ArH), 6.70 (dd, J = 8.9, 1.9 Hz, 1H, ArH), 4.05–4.02 (m, 4H, OCH_2), 3.98 (t, J = 6.5 Hz, 2H, OCH_2), 1.86–1.76 (m, 6H, CH_2), 1.53–1.45 (m, 6H, CH_2), 1.43–1.33 (m, 10H, CH_2), and 0.92 (t, J = 6.5, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.21 (d, J = 246.9 Hz, F–C), 161.47, 161.43, 160.28 (d, J = 246.9 Hz, F–C), 159.99, 159.91, 159.30, 142.39 (CH) 142.36 (CH), 135.27, 135.24, 131.92, 131.54, 130.96, 130.92, 130.53, 130.51, 130.47, 130.44, 126.34, 126.24, 126.20, 120.31 (d, J = 15.6 Hz, ArC), 118.47 (CN), 115.45 (d, J = 15.6 Hz, ArC), 115.09, 111.02, 111.00, 107.55 (C), 107.50, 102.76, 102.55 (ArC), 68.56, 68.43, 68.36 (OCH_2), 31.71, 29.59, 29.41, 29.33, 29.25, 26.13, 25.83, 22.75 (CH_2), and 14.19 (CH_3).

2.3. Compound *d*

Yield (25%), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.7, 2.0 Hz, 4H, ArH), 7.71 (s, 4H, ArH), 7.51 (s, 2H, CH), 7.49–7.43 (m, 4H, ArH), 7.29 (t, J = 8.7 Hz, 2H, ArH), 7.13–7.08 (m, 4H, ArH), 6.98 (dd, J = 8.7, 2.0 Hz, 4H, ArH), 6.80–6.73 (m, 2H, ArH), 6.70 (dd, J = 8.7, 2.0 Hz, 2H, ArH), 4.04 (t, J = 6.5 Hz, 4H, OCH_2), 3.98 (t, J = 6.5 Hz, 4H, OCH_2), 1.86–1.77 (m, 8H, CH_2), 1.54–1.44 (m, 8H, CH_2), and 1.39 (m, 12H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.44 (d, J = 251.2 Hz, F–C), 161.49, 161.44, 160.28 (d, J = 251.2 Hz, F–C), 160.00, 159.92, 159.57, 159.31, 154.88, 154.79, 142.38 (CH), 135.26, 133.64, 131.93, 131.82, 131.55, 131.02, 130.97, 130.93, 130.74, 130.53, 130.48, 130.45, 129.72, 126.44, 126.36, 126.25, 120.71, 120.32(d, J = 14.9 Hz), 118.48 (CN), 115.74, 115.56 (d, J = 14.9 Hz), 115.37, 115.10, 114.74, 111.03, 111.01, 110.62, 107.57 (C), 102.76, 102.55, 102.09, 101.86, (ArC), 69.70, 68.56, 68.38, 68.28, 29.86, 29.59, 29.56, 29.52, 29.41, 29.39, 29.34, 29.26, 29.09, 29.03, 26.13, and 26.04 (CH_2).