Journal of Photochemistry and Photobiology A: Chemistry 210 (2010) 130–139

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Oligofluorene blue emitters for cholesteric liquid crystal lasers

L.S. Chinelatto Jr[a], J. del Barrio[a], M. Piñol[a], L. Oriol[a,*], M.A. Matranga[b], M.P. De Santo[b,**], R. Barberi[b]

[a] Departament de Química Orgánica, Facultad de Ciencias-ICMA, Universidad de Zaragoza-CSIC, Pedro Cerbuna 12, 50009-Zaragoza, Spain
[b] CEMIF.CAL, INFM CNR-Licryl Lab., Physics Department, University of Calabria, 87036 Rende (Cs), Italy

ARTICLE INFO

Article history:
Received 19 October 2009
Received in revised form
30 December 2009
Accepted 8 January 2010
Available online 18 January 2010

Keywords:
Oligofluorenes
Luminescent materials
Cholesteric liquid crystals
Photonic band gap materials
Lasers

ABSTRACT

We present the synthesis and characterization of an oligofluorene series whose chemical structure has been tuned to have amorphous nature, compatibility with liquid crystalline matrices and intrinsic chirality. Oligofluorenes are good blue emitters and the emission quantum yield is around 0.8 in the violet-blue range. The prepared materials are suitable for mirror-less laser applications based on a dye-doped liquid crystal resonator. We propose to use fluorene-based compounds to combine two necessary properties to achieve laser emission from cholesteric liquid crystal mixtures: chirality and luminescence. A good intensity emission and a fine tuning of the laser emission are demonstrated.

1. Introduction

π-Conjugated organic materials have been intensively pursued for electronics, photonics and opto-electronics. From all conjugated systems, oligofluorenes and polyfluorenes have been identified as ideal candidates for many of these applications because of their efficient blue emission, both under photo- and electric stimulation, their thermal and chemical stability but also for their potential liquid crystalline properties. In fact, many systematic structure–activity reports can be found in the literature that show the versatility of fluorene compounds in the sense that the chemical structure of the aromatic core can be easily tailored to tune a variety of properties such as colour of the emission, electronic properties or liquid crystallinity [1–4].

For sometime, we have been interested in investigating fundamental opto-electronic and photonic properties of oligofluorenes and polyfluorenes. Therefore, in addition to the primary structure–activity studies, results on liquid crystalline networks with linearly polarized blue emission from fluorene-based mono- and dimethacrylates have been reported. The films were prepared by *in situ* photopolymerization of non-emissive reactive liquid crystalline matrixes containing reactive fluorene emitters [5–7]. Also, we have verified that fluorene-based materials are ideal, due to their high quantum yield and their liquid crystals compatibility, to be used as photoluminescent dyes in mirrorless lasers technology to obtain bright laser emission in the blue-violet range [8].

Cholesteric liquid crystals (CLCs) may be considered as unidimensional photonic crystals. Since liquid crystals are highly birefringent media, the helicoidal structure present at CLCs causes a periodical modulation of the refractive indices and the presence of a selective reflection band for light propagating along the helix axis, $\Delta\lambda = p\Delta n$, where p is the helical pitch and Δn the birefringence of the medium. A comprehensive analysis of a CLC as a photonic crystal is given in the review by Kopp et al. [9].

Doping cholesterics with photoluminescent dyes is considered as a very promising way for creating compact distributed feedback lasers. In dye doped cholesteric liquid crystal (DD CLC) lasers, the cholesteric liquid crystal acts as a resonator in laser emission from doped luminescent molecules [10,11]. It is important for the development of compact lasers that the major functional elements of a mirror-less laser are combined in one cell: active medium, cavity, and tunable selector.

The existence of the selective reflection band and the ability to change smoothly the selective reflection wavelength over a wide range under the action of applied external forces make it possible to design broad band tunable lasers based on DD CLCs. In particular, tunability of lasing can be achieved in several ways: varying the temperature [11], applying a mechanical stress [12] or an electric field [13], using photo-transformation effects [14,15] and by

* Corresponding author. Tel.: +34 976762276; fax: +34 976762686.
** Corresponding author.
E-mail addresses: loriol@unizar.es (L. Oriol), desanto@fis.unical.it (M.P. De Santo).

1010-6030/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2010.01.006

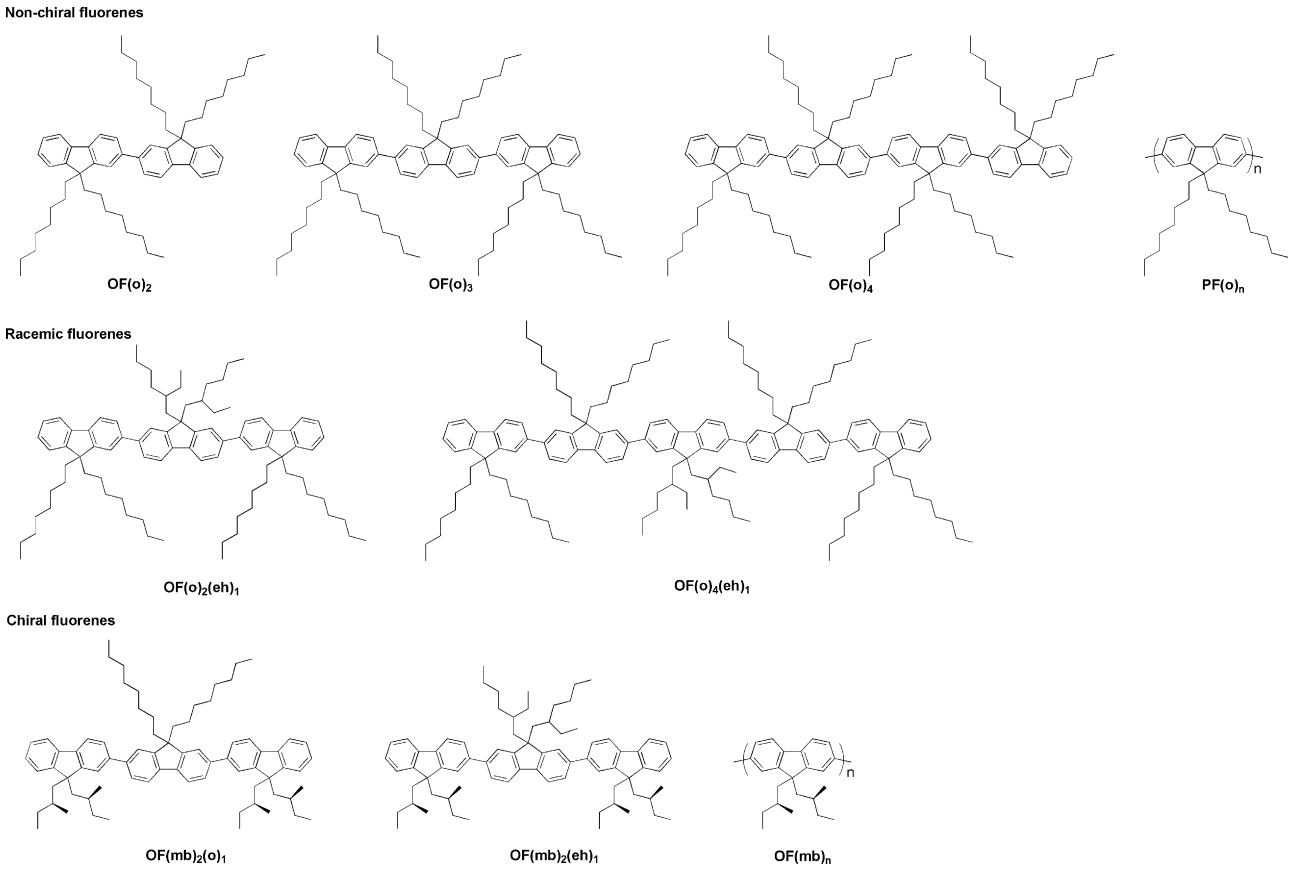

Fig. 1. Structure of the investigated oligofluorenes and polyfluorenes.

assembling cells with pitch gradient and with spatial distribution of different dyes [16,17].

It is possible to readily obtain tunable laser in the near ultraviolet through the visible spectrum to the near infrared. The broad wavelength tuning range of LC lasers, coupled with their microscopic size, narrow linewidths (<0.1 nm), and high optical efficiencies as compared with more conventional solid-state lasers, open up new applications in areas such as labs-on-a-chip, medical diagnostics, dermatology and cosmetics.

In this work we have undertaken the synthesis of a series of monodispersed oligofluorenes, both homo-oligofluorenes and co-oligofluorenes, from a dimer to a pentamer (see Fig. 1) and investigated their possible application on mirrorless lasing. In addition, we have prepared an oligomer, **OF(mb)$_n$**, of polydispersed nature and a polymer, **PF(o)$_n$** whose synthesis and properties have already been described by other authors [18]. Each fluorene unit has been functionalized at the C9 position with two pendant alkyl chains, which is critical for attaining adequate solubility and thermal behaviour. In these structures, the pendant aliphatic chains have been varied from linear to branched ones, either racemic or chiral. In terms of promoting mesomorphism, it has been proven that it is necessary to combine at least 4 fluorene units with appropriate aliphatic chains at the C9 bridging position of fluorenyl units [19]. The benefit from branching aliphatic pendant chains in comparison to linear ones has also been proved in terms of mesophase formation and crystallinity suppression. In addition, the incorporation of chirality in these aliphatic chains has been reported to give rise to helical assemblies and to cause chiroptical activity in films [20,21]. Regardless of pendant aliphatic chains, co-oligomers are more favourable to the formation of morphologically stable glassy nematics than homo-oligomers [19].

At present, DD CLCs contain at least three compounds: a nematic material, an optical active dopant and a luminescent dye, that have to be carefully selected according to their optical, solubility and thermal stability properties. Therefore, we envisaged the possibility to use fluorene-based materials that can act at the same time as chirality promoters and luminescent compounds [8]. For this purpose, we have focussed our attention mainly on those oligomers containing laterally appended chiral chains. We prove that the investigated compounds have high emission quantum yields and adequate stability. In addition, fluorenes are optically dichroic molecules in which the emission transition moments aligns within the long molecular axis [5]. Takezoe and co-workers [22,23] have shown that doping a chiral liquid crystal with a polymeric dye helps in suppressing fluctuations in the LC matrix, enhancing the order parameter. Moreover, this promotes high alignment of the transition dipoles with the local liquid crystal director, lowering the lasing threshold. In our case, the fluorene-based emitters are of oligomeric nature with scarcely tendency towards crystallization. The thermal behaviour and twisting power ability can be adjusted by structural chemical changes such as the aromatic core length and the structure of the appended lateral chain. Therefore, we show how they can be used to obtain a tuning of the laser emission.

2. Experimental

2.1. Chemicals

Chemicals and reagents were used as received from their commercial sources. Toluene, and *N,N*-dimethylformide (DMF) were dried using standard procedures. Tetrakis(triphenylphosphine) palladium(0) [$Pd(PPh_3)_4$], bis(1,4-cyclooctadiene)nickel(0) [Ni-