Synthesis and Properties of 2-Phenylbenzoxazole-Based Luminophores for *in situ* Photopolymerized Liquid-Crystal Films

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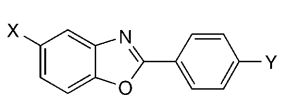
We report the synthesis of a series of blue-emitting 2-phenylbenzoxazoles (PBOs) substituted at either the 5- or 6-position of the benzoxazole ring and the *para*-position of the phenyl substituent. The thermal and optical properties of the materials can be rationalized in terms of the position of the substituent at the benzoxazole moiety and the electron-withdrawing or electron-donating character of the substituents. From the results, we conclude that the combination of an electron-donating substituent at the benzoxazole fragment and an electron-withdrawing one at the phenyl fragment has a more marked effect on the electronic properties of the aromatic PBO core than other possibilities. This particular combination gives luminophores that are suitable for optical applications on the basis of their high emission efficiency and photostability. In view of that, oriented films were prepared by *in situ* polymerization of a mixture of a liquid crystalline direactive matrix containing 5% (*w*/*w*) of the luminophore. The films exhibit linearly polarized emission.

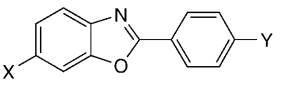
1. Introduction. – In the last few years, there has been increasing interest in the field of polarized-light-emitting-layers because these systems can provide the linearly polarized emission that is needed for liquid-crystal displays (LCDs), thus simplifying their manufacture and reducing costs [1][2]. Linearly polarized light emission can be obtained from thin films with optically anisotropic emitters oriented in a specific direction [3]. From the point of view of structural order, self-organizing liquid crystals offer excellent control over molecular orientation through the use of appropriate processing techniques. A feasible approach to prepare a film that actively emits polarized light is based on the incorporation of a luminophore into a liquid-crystal matrix, in which it aligns as a result of the guest-host effect. Molecular orientation needs to be preserved, and *in situ* photopolymerization of oriented reactive liquid-crystal monomers provides an excellent and fast way to produce permanently cross-linked thin anisotropic polymeric films [4]. This strategy has already been successfully applied to the production of oriented luminescent films in which the luminophore has been dispersed in, or covalently bound to, the matrix [5–8]. A number of factors control the potential applications of a practical luminophore, and these include its compatibility with the liquid-crystal matrix and its thermal and photochemical stability. Therefore, for practical applications, the design and synthesis of suitable organic luminophores is still required.

In the search for new luminophores for use in anisotropic emissive thin films, we have given consideration to the benzoxazole core because of its attractive optical properties and potential mesogenicity. Benzoxazoles are a group of heterocyclic compounds that have attracted considerable interest because they are known as photostable and highly efficient luminophores used as organic brightening agents, laser dyes, organic-plastic scintillators, and optical-fiber sensors [9][10]. The fact that the luminescence of this system is greatly influenced by substituents has also found applications, and polymers with pendant 2-phenylbenzoxazole (PBO) systems have been used in the generation of fluorescent images by photolithographic methods or as chemosensors for metal ions [11][12]. Furthermore, several 2-phenylbenzoxazoles have been studied as blue emitters in electroluminescence devices [13][14] and second-order NLO-active chromophores (NLO = nonlinear optics) [15–19].

In this paper, we present the synthesis and properties of a series of blue-emitting doubly substituted PBOs (*Fig. 1*). We focused our attention on PBOs with substituents at both the benzoxazole moiety and the phenyl ring, and structural modifications were aimed at tailoring the thermal and optical properties to obtain effective liquid-crystalline-compatible luminophores. The incorporation of suitable substituents at the PBO core is a basic characteristic to obtain liquid-crystal phases and, for this reason, an initial screening of potential substituents was performed to identify their ability to promote mesophase formation. However, the ultimate choice of substituents was made by considering their effect on the optical and photophysical properties of the PBO derivative. Therefore, electron-donating and electron-withdrawing substituents at the 5- or 6-positions of the benzoxazole moiety and at the *para*-position of the phenyl ring were combined to investigate their effect on the absorption/emission properties and photostability of these systems. The target compounds are represented as *n*X-PBO-Y where PBO represents the 2-phenylbenzoxazole core, X is the substituent at either the 5- or 6-position ($n = 5$ or 6, resp.) of the benzoxazole moiety, and Y is the substituent at the phenyl ring.



5HexO-PBO-OHex	X = $C_6H_{13}O$	Y = $C_6H_{13}O$
5HexO-PBO-CN	X = $C_6H_{13}O$	Y = CN
5HexO-PBO-COOHex	X = $C_6H_{13}O$	Y = $C_6H_{13}OCO$
5NC-PBO-OHex	X = CN	Y = $C_6H_{13}O$
5HexOOC-PBO-OHex	X = $C_6H_{13}OCO$	Y = $C_6H_{13}O$

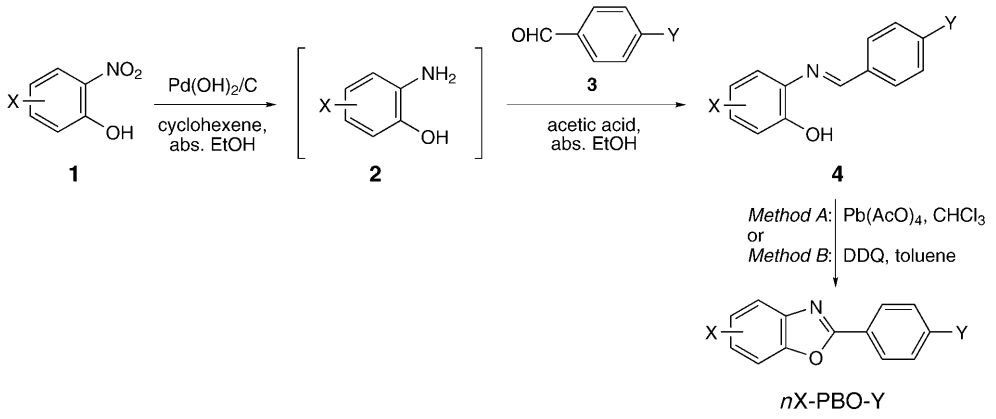


6HexO-PBO-OHex	X = $C_6H_{13}O$	Y = $C_6H_{13}O$
6HexO-PBO-CN	X = $C_6H_{13}O$	Y = CN
6HexOOC-PBO-OHex	X = $C_6H_{13}OCO$	Y = $C_6H_{13}O$

Fig 1. *Chemical Structure and Nomenclature of the Synthesized Benzoxazoles*

2. Results and Discussion. – 2.1. *Synthesis and Liquid-Crystalline Properties of the Benzoxazoles.* The synthesis of the benzoxazoles was approached by ring closure of the intermediate imines under oxidative conditions. The general procedure outlined in *Scheme 1* proved to be quite versatile. Condensation of a 2-aminophenol **2**, carrying the substituent X at the 4- or 5-position, with a benzaldehyde **3**, carrying the substituent Y at the 4-position, yielded the imine precursor **4** under acidic conditions. Initially, the

Scheme 1. *General Synthetic Procedure for the Preparation of the Benzoxazoles*



oxidative cyclization of the imine was undertaken with lead(IV) acetate (*Method A*, *Scheme 1*). However, yields were significantly higher on using DDQ (4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile) in toluene (*Method B*, *Scheme 1*).

The main problem encountered in the specific application of this strategy is the availability of the starting 2-nitrophenol **1**. For instance, when 5-(hexyloxy)-substituted benzoxazoles (5HexO-PBO-Y) were desired, attempts were made to prepare the required 4-(hexyloxy)-2-nitrophenol by nitration of 4-(hexyloxy)phenol [20]. However, numerous by-products were obtained, and these proved difficult to separate and led to a low yield (46%) of the desired product. The alternative route outlined in *Scheme 2* was used to obtain from **5** the benzoxazoles **6** with a benzoyl-protected OH group. After deprotection to **7**, subsequent alkylation under *Williamson* conditions furnished the desired POBs [21]. Nitration of 4-hydroxyphenyl benzoate to yield the 2-nitrophenol intermediate **5** proved to be an efficient process and gave the required product in 83% yield.

The thermal behavior of the benzoxazoles was investigated by optical microscopy (OM) and differential scanning calorimetry (DSC). The results are summarized in *Table 1*. The PBO moiety substituted at the 5- or 6-position is a planar aromatic system, at least formally, structurally related to the well known *p*,*p*′-disubstituted benzylideneaniline mesogens [22] in which the exocyclic C=N bond is constricted into a new heterocycle by an O-bridge. Fixation of the structure improves the photoluminescence stability but disturbs the desirable molecular linearity required for the formation of calamitic mesophases. Nevertheless, the potential of the PBO moiety to promote liquid crystallinity has been proven in both low- and high-molecular-mass compounds [20] [21] [23–25].

The results collected in *Table 1* show that substitution at the 5-position is more favorable to the induction of mesogenicity than substitution at the 6-position, a trend that has previously been pointed out by *Pavluchenko et al.* [23]. To support this experimental observation, we performed geometrical calculations on the PBO structure previously optimized by molecular mechanics (MM2) and semi-empirical (MOPAC-AM1)

Scheme 2. *Synthesis of the 5-(Hexyloxy)benzoxazoles*

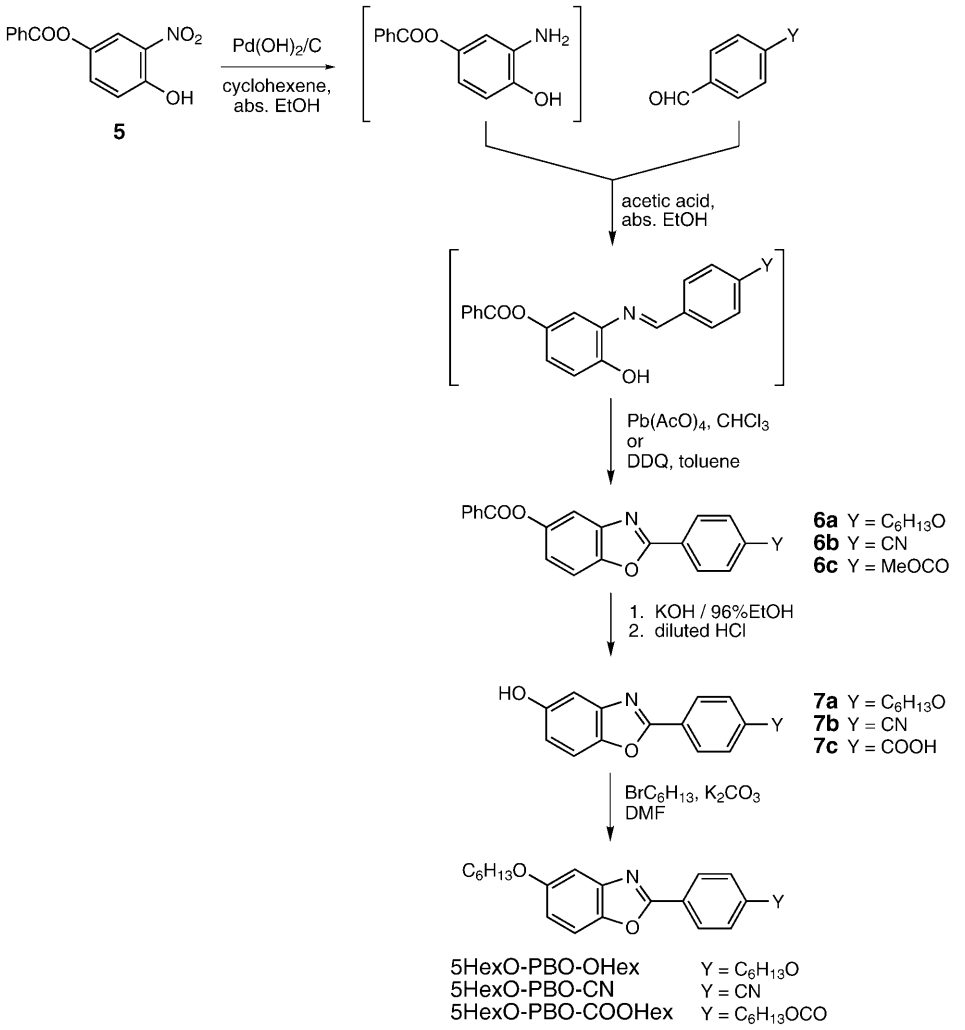


Table 1. *Thermal and Thermodynamic Data for the Benzoxazoles*

	Transition temperatures [°][a])		Transition temperatures [°][a])
5HexO-PBO-OHex	Cr 59 N 78 I[b])	5HexOOC-PBO-OHex	Cr 97 (SmA 78) I[c])
5HexO-PBO-CN	Cr 102 (N 95)[d]) I	6HexO-PBO-OHex	Cr 45 (N 42) I[e])
5HexO-PBO-COOHex	Cr 82 I	6HexO-PBO-CN	Cr 98 I
5NC-PBO-OHex	Cr 142 I	6HexOOC-PBO-OHex	Cr 82 I

[a]) Cr = crystal phase, N = nematic phase, SmA = smectic A phase, I = isotropic liquid; monotropic transition in parenthesis. [b]) $\Delta H_{N\text{-}I}$ is 0.76 kJ mol^{-1}. [c]) $\Delta H_{SmA\text{-}I}$ is -5.42 kJ mol^{-1}. [d]) Temperature determined by optical microscopy. [e]) $\Delta H_{N\text{-}I}$ is -0.48 kJ mol^{-1}.

calculations, and it was found that deviation from linearity depends on the disubstitution pattern at the benzoxazole moiety (*i.e.*, 2,5 *vs.* 2,6). Geometrical calculations indicate that the 2,5-substitution pattern has a deviation from linearity of 24°, while the 2,6-substitution pattern gives rise to a deviation of 35.5° (*Fig. 2*).

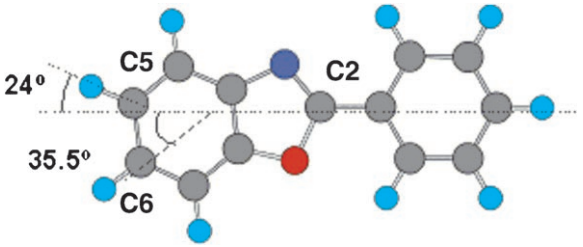


Fig. 2. *Linearity deviation of the 2,5-substitution pattern and 2,6-substitution pattern in PBO calculated for the structure optimized by molecular mechanics* (MM2) *and semiempirical* (MOPAC-AM1) *calculations*

Table 2. *Optical Properties of Investigated Benzoxazoles in THF*

	Substitution X/Y[a])	λ_{abs} [nm] (log ε [M^{-1} cm^{-1}])	λ_{em} [nm]	ϕ_{em}
PBO		299 (4.42)	338, 353	0.49
5HexO-PBO-OHex	D/D	324 (4.38)	370, 382	0.41
5HexO-PBO-CN	D/A	336 (4.22)	438	0.70
5HexO-PBO-COOHex	D/A	332 (4.26)	430	0.67
5NC-PBO-OHex	A/D	312 (4.56)	355, 368 (sh)	0.50
5HexOOC-PBO-OHex	A/D	312 (4.44)	350, 365	0.51
6HexO-PBO-OHex	D/D	320 (4.56)	365, 382	0.47
6HexO-PBO-CN	D/A	340 (4.48)	417	0.90
6HexOOC-PBO-OHex	A/D	320 (4.66)	368, 379 (sh)	0.50

[a]) Electronic character of the substituents X and Y: A = electron-accepting and D = electron-donating.

The mesomorphic properties are also affected by swapping the substituents at the benzoxazole and phenyl fragments. For instance, 5HexO-PBO-CN shows a monotropic nematic mesophase at 95° but its isomer 5NC-PBO-OHex has a higher melting point and does not show mesomorphism. For the esters 5HexO-PBO-COOHex and 5HexOOC-PBO-OHex, only the incorporation of the ester group at the benzoxazole moiety gives rise to a mesophase, with a monotropic smectic A mesophase observed at 78°.

2.2. *Optical Properties and Photostability.* The absorption and emission spectra of the 2-phenylbenzoxazoles were recorded in THF solution (see *Table 2*). The UV/VIS spectrum of PBO, taken as a reference, presents a distinct structured absorption band centered at *ca.* 300 nm along with a structured emission band in the UV region (354 nm). The fluorescence quantum yield is 0.49, which is comparable to that of quinine sulfate.

The absorption and emission properties of PBO and some of its derivatives are well documented [10][26–30]. Publications on this conjugated aromatic system mostly con-

cern the incorporation of substituents at the phenyl ring and conclude that the photophysical behavior can be dramatically affected. For example, a strong red-shifted fluorescence enhancement is observed when electron-donating substituents are located at the *para*-position of the phenyl ring because of an intramolecular charge transfer in the excited state from the phenyl ring to the benzoxazole electron-withdrawing moiety. This phenomenon is the result of a partial C=C bond between the benzoxazole and phenyl fragments, which restricts rotation of the two aromatic subunits of 2-phenylbenzoxazole.

In this study, we prepared doubly substituted 2-phenylbenzoxazoles and, depending on the electron-accepting (A) or electron-donating (D) ability of the substituents, several combinations were investigated; these systems are denoted in *Table 2* as X/Y = D/D, D/A, or A/D. Substitution gives a systematic bathochromic shift of the absorption that depends on the electronic nature of the substituents. Benzoxazoles with a D/A substitution present the largest bathochromic shift with a broad and featureless absorption band. However, benzoxazoles with an A/D-type substitution pattern show the smallest bathochromic shift and an absorption band with a vibrational structure similar to that of PBO. Benzoxazoles with a D/D pattern show a behavior that is intermediate between the two systems outlined above.

As far as the emission is concerned, comparison of the different systems reveals a similar trend in terms of the position and shape of the emission bands as found for the absorbance. The D/A combination gives the largest bathochromic shift in the emission, with broad and featureless bands located above 415 nm in the violet-blue region of the spectrum. These systems are also the most efficient luminophores, with quantum yields ranging from 0.65 to 0.90. In contrast, benzoxazoles of the A/D-type show emission bands in the range 355–370 nm, which is close to that of PBO. These bands also have a weak vibronic structure similar to PBO. Once again, D/D-type benzoxazoles show an intermediate type of behavior.

In relation to the position of the substituent at the benzoxazole moiety, benzoxazoles substituted at the 6-position show higher molar absorption coefficients than the related 5-substituted isomers. This is certainly due to the fact that the substituent at position 6 of the benzoxazole is in a resonance position with respect to the N-atom of the heterocycle.

The optical properties of the materials in cyclohexane were also examined. The low solvent polarity leads to almost identical absorption wavelengths and molar absorption coefficients but the bands are, in general, more structured in cyclohexane than in THF. However, the emission spectra show substantial differences. In general, emission bands appear at shorter wavelengths in cyclohexane than in THF and have more pronounced vibronic features. The strongest solvatochromism is observed for D/A benzoxazoles. It is known that polar excited states are stabilized by polar solvents and give broad emission bands, a fact that suggests that the excited states of D/A benzoxazoles are more polar than the others.

The results show that optical behavior depends on the substituents and, in this respect, A/D and D/D benzoxazoles resemble PBO more closely than D/A benzoxazoles, which are the most suitable luminophores in terms of their efficiency and wavelength emission.

Evaluation of the photochemical stability is a critical issue from the point of view of potential applications. For this reason, the photostability of the benzoxazoles was determined in $CHCl_3$ solution and in PMMA (poly(methyl methylacrylate)) films. The samples were irradiated with 325-nm light, and changes in the UV/VIS spectra were recorded. The photostability was assessed on the basis of the energy required to decrease the absorbance to 90% of its original value at 325 nm, and this value is referred to as E_{90}. The relevant data are collected in *Table 3*.

Table 3. *Photostability Data for the Benzoxazoles in $CHCl_3$ Solution and in a PMMA Matrix*

	E_{90} [J cm^{-2}]			E_{90} [J cm^{-2}]	
	$CHCl_3$ solution	PMMA film		$CHCl_3$ solution	PMMA film
5HexO-PBO-OHex	3	15	5HexOOC-PBO-OHex	9	21
5HexO-PBO-CN	[a])	36	6HexO-PBO-OHex	0.1	2
5HexO-PBO-COOHex	[a])	68	6HexO-PBO-CN	95	70
5NC-PBO-OHex	39	27	6HexOOC-PBO-OHex	84	25

[a]) The photodegradation was not significant up to absorbed energy values of 100 J cm^{-2}.

The values obtained show that the photostability is also dependent on the electronic character and position of the substituents. It is interesting to point out the remarkable stability of the 5D-PBO-A type benzoxazoles in solution. Up to an irradiation dose of 100 J cm^{-2}, degradation of the chromophores was almost insignificant. In contrast, the fastest degradation was observed for D/D systems regardless of whether it was substituted at the 5- or 6-position of the benzoxazole moiety. The spectral changes under irradiation at 325 nm are shown in *Fig. 3* for 5HexOOC-PBO-OHex and 5HexO-PBO-OHex as representative examples. In the first case, a gradual decrease in the maximum absorbance takes place with an increase of the absorbance above 330 nm, and an isosbestic point is observed at 335 nm. For 5HexO-PBO-OHex, the spectral changes are more marked, and the absence of isosbestic points indicates the simultaneous occurrence of more than one photoreaction.

PBOs immobilized in a PMMA matrix were found to have a different photostability from that of the corresponding system in solution (*Fig. 4*). The absorbance maxima were recorded at the same wavelength as in solution, *i.e.*, disregarding the formation of aggregates, but E_{90} values are manifestly different in most cases. The stability under illumination follows the same trend as in solution, with the D/A system being the most photostable and D/D the least stable. Nevertheless, in this case, the photostability of 5D-PBO-A is comparable to the rest of the PBO systems. In general, PBOs of the D/A and A/D type are more stable in solution, but the D/D systems are up to one order of magnitude more stable in PMMA films.

2.3. *Anisotropic Emissive Films.* Studies published by *Catalán et al.* on PBOs have established that the ground state and the excited state are almost coplanar, and that the π–π^* transition is polarized along the longitudinal axis of the molecule [27]. The fact that these systems exhibit direction-dependent absorption of light is of basic inter-

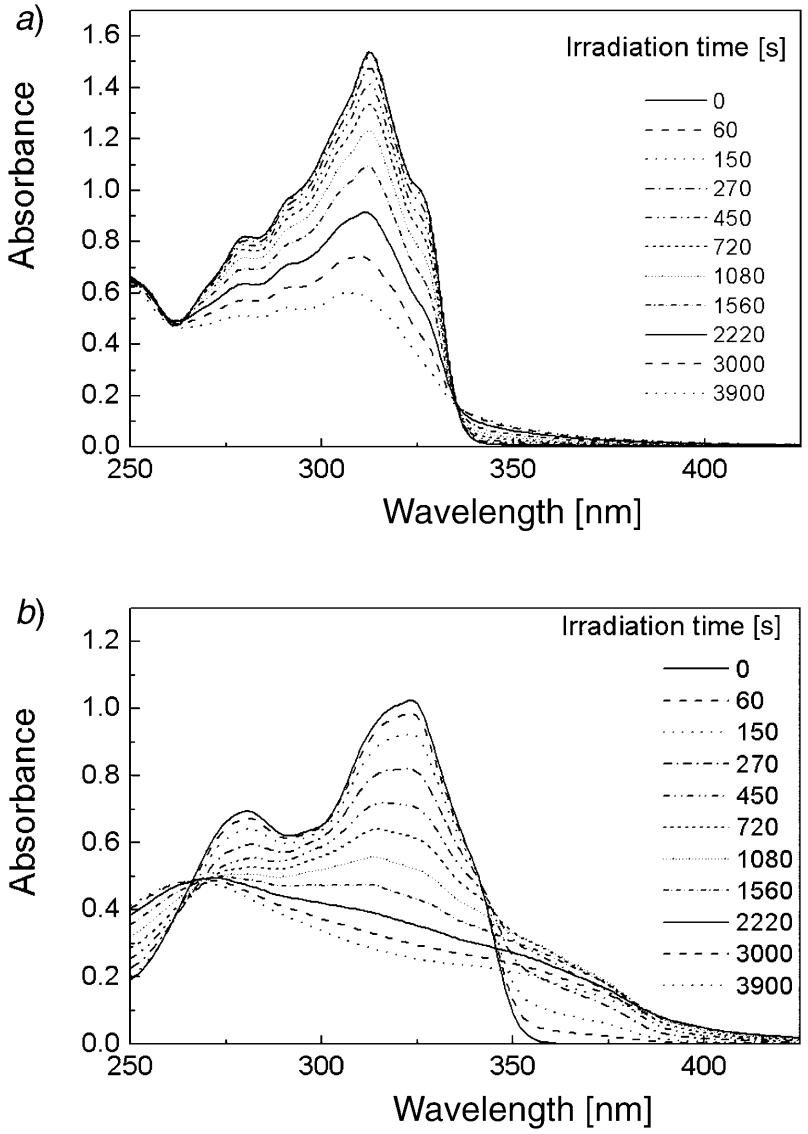


Fig. 3. *UV/VIS Spectra* ($CHCl_3$) *at different irradiation times for* a) *5HexOOC-PBO-OHex and* b) *5HexO-PBO-OHex*

est for studies on oriented materials, and they are attractive candidates as emissive guests in oriented liquid-crystalline networks.

Therefore, to evaluate the potential of these systems for polarized luminescence, oriented networks were prepared by *in situ* photopolymerization of a direactive non-luminescent liquid crystal, C6M, doped with 5% (weight) of the luminophore. It has been reported that highly cross-linked films show lower dichroic ratios than films

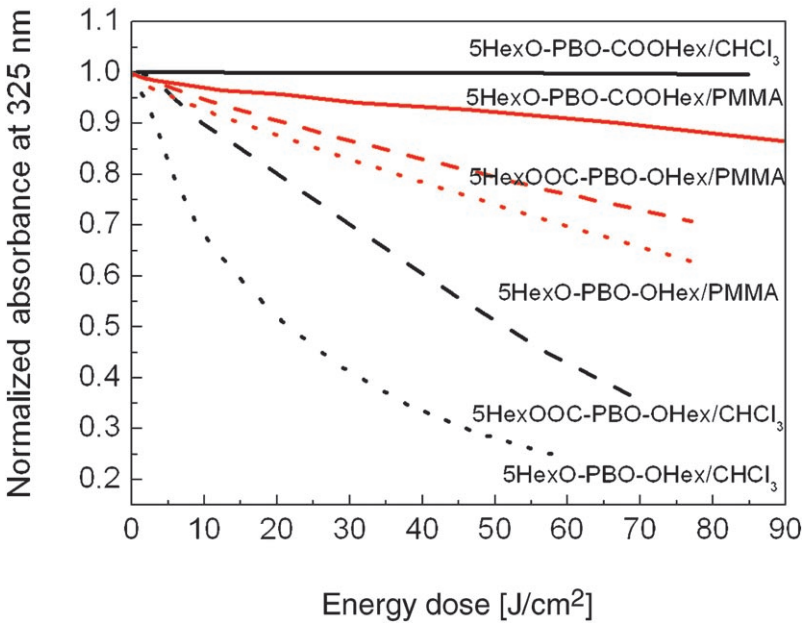


Fig. 4. *Plot of the normalized absorbance at 325 nm* vs. *the absorbed energy for 5HexOOC-PBO-OHex, 5HexO-PBO-COOHex, and 5HexO-PBO-OHex in $CHCl_3$ solution and PMMA films*

with low levels of cross-linking but their properties are almost temperature-independent, and luminescence is thermally stable and photostable [6][7].

The reactive liquid-crystal mixtures were polymerized in the nematic phase between 90 and 100°. Polymerization temperatures were selected according to the mesomorphic properties of these mixtures, which were investigated by OM with appropriate light filters. The liquid-crystalline behavior of the mixtures was comparable to that of C6M, the major component of the blend, which has a nematic phase in the range 86–116°. All the reactive mixtures developed a nematic phase above 78° and were completely miscible. Prior to the production of oriented films, the photopolymerization of the blends was studied by photo-DSC to rule out any effect of the luminophore on the isothermal photoinitiated polymerization of the reactive liquid-crystal matrix. C6M does not absorb above 350 nm but some of the PBOs still have some residual absorption at 365 nm, the wavelength of the emission of the lamp, and might reduce the efficacy of the photoinitiator I-651, which also absorbs at this wavelength. The samples were heated to the selected temperature and irradiated with 365-nm light during 15 min. From the registered DSC scan, it was verified that photoinduced polymerization proceeds rapidly during the first few seconds of exposure to light. Assuming a polymerization enthalpy equal to 78 kJ mol^{-1}, conversion degrees of 80–90% were calculated from the integration of the polymerization exotherm.

Oriented thin films were obtained by carrying out the photopolymerization in commercial glass cells with unidirectionally rubbed polyimide coatings for planar alignment. These cells were filled with the reactive mixtures by capillary action. In the

course of polymerization, a transparent film of good optical quality and a single domain structure with good planar orientation was obtained, as observed by optical microscopy. Polarized UV/VIS spectroscopy was used to establish the orientation of the films; however, studies were complicated because the absorption of the glass cell is superimposed to the absorption of the C6M matrix and, to some extent, to the luminophores. Therefore, absorption was maximum along the rubbing in the cell and minimum along the perpendicular to it. Dichroic ratios in absorption of *ca.* 3 were determined.

The emission properties determined for the different benzoxazoles are collected in *Table 4*. It can be observed that there is good agreement between the emission wavelengths determined in the oriented films and those in solution and PMMA. In general, broad and unresolved emission bands were registered for the solid films in comparison to the spectra in solution, especially for A/D and D/D benzoxazoles, presumably because of intermolecular interactions arising in the ordered solid phase. Accidental photodegradation of the PBO luminophores during photopolymerization was not apparent from the emission spectra.

Table 4. *Emission Wavelength and Dichroism of the Anisotropic Polymeric Films*

	λ_{em} [nm]	R_{em} [$I_{\parallel}/I_{\perp}$]		λ_{em} [nm]	R_{em} [$I_{\parallel}/I_{\perp}$]
5HexO-PBO-OHex	388	3.4	5HexOOC-PBO-OHex	372	4.0
5HexO-PBO-CN	431	3.4	6HexO-PBO-OHex	375, 392	2.5
5HexO-PBO-COOHex	427	3.3	6HexO-PBO-CN	427	3.0
5NC-PBO-OHex	377	4.0	6HexOOC-PBO-OHex	392	2.9

Furthermore, films exhibited the maximum emission when the polarization axis of the incident light was parallel to the preferential orientation direction in the cell ($I_{\parallel}$), and minimum when it was perpendicular to it ($I_{\perp}$) (*Fig. 5*). The dichroic ratios (R_{em}) were all in the range 3–4. Because the principal electronic axis of PBOs is aligned with the long molecular axis, the results show that there is a preferential orientation of the luminophore within the film along the rubbing direction in the cell.

Therefore, it can be deduced that the PBOs are introduced in a 'guest–host' configuration in anisotropic films obtained by *in situ* photopolymerization of reactive liquid crystal and that such a system actively produces linearly polarized light. Nevertheless, 6-substitution gives lower emission dichroism, which can be tentatively related to the larger deviation of the molecular linearity for a 2,6-disubstitution pattern in the PBO core (see *Fig. 2*).

3. Conclusions. – In this work, the mesomorphic behavior and the absorption/emission characteristics of several doubly substituted 2-phenylbenzoxazole (PBO) derivatives were investigated. The PBOs were synthesized by oxidative ring closure of imines under very mild reaction conditions, which make it possible to incorporate a diverse range of substituents in the PBO core. The results show that tuning of the emission is possible depending on the electronic nature and position of the substituents at the PBO core. Amongst the various possibilities, an electron-donating substituent located at the 5- or 6-position of the benzoxazole moiety and an electron-withdrawing in the *para*-position of the phenyl ring is the best option in relation to the optical properties.

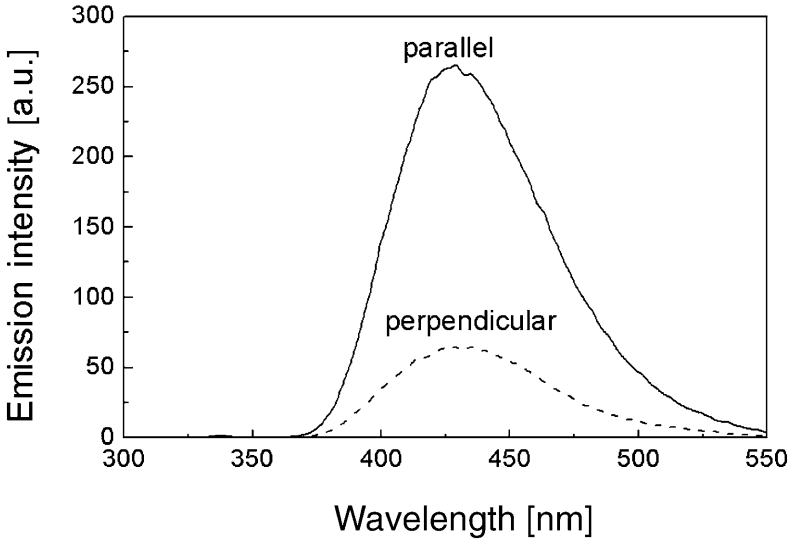


Fig. 5. *Polarized emission of the anisotropic film 5HexO-PBO-CN and C6M photopolymerized in a cell for planar alignment at 90° in the nematic phase*

Blue emission and quantum yields ranging from 0.60 to 0.90 are combined with suitable photostability in the solid state. The 5-substitution pattern gives larger bathochromic shifts but the 6-substitution produces a larger enhancement of the emission efficiency. In relation to the mesomorphic properties, the extent of the unfavorable bend in the molecular structure due to the presence of the benzoxazole ring depends on the substitution pattern, and 5-substitution at the benzoxazole is structurally more acceptable than the 6-substitution to promote mesomorphism in the PBO core.

In summary, D/A 5-substituted PBOs are suitable luminophores for obtaining polarized luminescence as they combine the structural requirements compatible with the formation of mesophases and appropriate emissive properties. These properties are transferred to solid anisotropic films obtained by an easy and clean method, the *in situ* photopolymerization of reactive low-molar-mass liquid crystals.

From the results we conclude that PBOs are very promising luminophores for the generation of linearly polarized light by using the auto-organization capability of liquid-crystalline media. These results have encouraged us to undertake further research regarding the incorporation of these systems in photo-addressable liquid crystals.

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Experimental Part

1. *General.* FC = Flash column chromatography. Optical microscopy (OM): *Olympus-BH-2* polarizing microscope equipped with a *Linkam-THMS* hot-stage central processor and a *CS196* cooling system. Differential scanning calorimetry (DSC): *DSC 2910* from *TA Instruments* with samples sealed in alumi-

nium pans; scanning rate of 10° min^{-1}; under N_2; temp. were read at the onset of the peak after prior heating of the sample to the isotropic liquid and cooling to 0°. UV/VIS Spectra: *UV4-200* spectrophotometer from *ATI-Unicam*; 10^{-5} M solns. in THF or cyclohexane. Emission spectra: *Perkin-Elmer LS50B* spectrofluorimeter; THF or cyclohexane solns. of *ca.* 0.01 absorbance (*ca.* 10^{-7} M) under excitation at the absorption maximum; emission quantum yields (ϕ_{em}) in THF relative to quinine sulfate in sulfuric acid as a reference ($\phi_{em} = 0.546$).

IR Spectra: *ATI-Matsson Genesis-FTIR* spectrophotometer; nujol mulls between NaCl disks; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Varian Unity-300* spectrometer; δ in ppm, J in Hz. Elemental analysis: *Perkin-Elmer 240C* microanalyzer.

2. *Syntheses.* 2.1. *2-Nitrophenols* **1**. *4-Hydroxy-3-nitrobenzonitrile* was purchased from *Aldrich*.

5-(Hexyloxy)-2-nitrophenol. A soln. of 3-(hexyloxy)phenol (prepared by a *Williamson* reaction between resorcinol (= benzene-1,3-diol) and 1-bromohexane; 4.0 g, 0.02 mol) in CH_2Cl_2 (48 ml) and Et_2O (100 ml) was added to a stirred mixture of $NaNO_3$ (1.7 g, 0.02 mol) in H_2O (24 ml) and conc. HCl soln. (18 ml). Ac_2O (2/3 drops) was added, and the mixture was stirred at r.t. for 4 h. The aq. layer was extracted with Et_2O, the combined org. extract washed with H_2O, dried ($MgSO_4$), and evaporated, and the crude oil purified by FC (hexane/AcOEt 10:1): 5-(hexyloxy)-2-nitrophenol (33%). Oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 11.02 (*s*, 1 H); 7.98 (*d*, $J = 10.3$, 1 H); 6.49–6.45 (*m*, 2 H); 3.99 (*t*, $J = 6.5$, 2 H); 1.82–1.72 (*m*, 2 H); 1.44–1.21 (*m*, 6 H); 0.90–0.85 (*m*, 3 H).

Hexyl 4-Hydroxy-3-nitrobenzoate. A mixture of 4-hydroxy-3-nitrobenzoic acid (7.4 g, 40.7 mmol) and $NaHCO_3$ (3.4 g, 40.7 mmol) in dry *N*,*N*-dimethylacetamide (50 ml) was heated under reflux until the evolution of CO_2 had ceased. Hexyl 4-methylbenzenesulfonate (8.06 g, 38.7 mmol; previously prepared by reaction of hexanol (1 equiv.) with 4-methylbenzenesulfonyl chloride (1.2 equiv.) at 0° in dry pyridine under Ar) was added, and the mixture was stirred and heated under reflux for 1 h. The mixture was allowed to cool down to r.t. the resulting soln. poured into H_2O, the mixture extracted with CH_2Cl_2 (3×50 ml), the extract washed with sat. aq. $NaHCO_3$ soln. and H_2O, the combined org. phase dried ($MgSO_4$) and evaporated, and the crude product purified by FC (silica gel, hexane/AcOEt 9:1): Oil (6.95 g, 67%). ^{1}H-NMR (300 MHz, $CDCl_3$). 10.85 (*s*, 1 H); 8.77 (*d*, $J = 2.1$, 1 H); 8.20 (*dd*, $J = 8.8$, 2.1, 1 H); 7.18 (*d*, $J = 8.8$, 1 H); 4.30 (*t*, $J = 6.7$, 2 H); 1.76–1.66 (*m*, 4 H); 1.42–1.20 (*m*, 4 H); 0.89–0.84 (*m*, 3 H).

Hexyl 3-Hydroxy-4-nitrobenzoate was prepared from 3-hydroxy-4-nitrobenzoic acid as described above for hexyl 4-hydroxy-3-nitrobenzoate: 56% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.45 (*s*, 1 H); 8.10 (*dd*, $J = 8.8$, 1.8, 1 H); 7.55 (*m*, 1 H); 4.31–4.26 (*m*, 2 H); 1.99–1.68 (*m*, 2 H); 1.43–1.23 (*m*, 6 H); 0.84 (*m*, 3 H).

2.2. *4-Substituted Benzaldehydes* **3**. *4-(Hexyloxy)benzaldehyde* and *4-formylbenzonitrile* were obtained from *Aldrich*.

Methyl 4-Formylbenzoate. Conc. H_2SO_4 soln. (5.5 ml) was added to a soln. of 4-formylbenzoic acid (4.0 g, 26.6 mmol) in MeOH (250 ml), and the mixture was heated under reflux for 24 h. The resulting soln. was allowed to cool down to r.t., poured into 10% HCl soln. (150 ml), and stirred for 1 h. The solvent was evaporated and the residue extracted with CH_2Cl_2. The combined org. extract was successively washed with aq. $NaHCO_3$ soln., H_2O and brine, dried ($MgSO_4$), and evaporated and the crude product purified by recrystallization from 96% EtOH: crystalline white solid (2.4 g, 55%). ^{1}H-NMR (300 MHz, $CDCl_3$): 10.06 (*s*, 1 H); 8.15 (*d*, $J = 9.0$, 2 H); 7.91 (*d*, $J = 9.0$, 2 H); 3.92 (*s*, 3 H).

2.3. *Intermediate Imines* **4***: General Procedure.* A soln. of the appropriate 2-nitrophenol in abs. EtOH and cyclohexene (*ca.* 45 ml/g of the nitro derivative) was heated under reflux with stirring. Then 20% (*w*/*w*) $Pd(OH)_2$/C (*ca.* 30% of the weight of the nitro derivative) was added under Ar. The mixture was protected from light, and the progress of the reaction was followed by TLC. After consumption of the starting material (*ca.* 4 h), the mixture was allowed to cool down to r.t. and filtered through a pad of *Celite*®. The solvent was evaporated to give the 2-aminophenol **2** as an oil. This oil was dissolved in abs. EtOH and added under Ar to a soln. of the appropriate benzaldehyde in abs. EtOH. The mixture was stirred and heated for 12 h under reflux in the presence of a catalytic amount of AcOH. The resulting soln. was then evaporated and the product recrystallized from abs. EtOH to give **4**.

2.4. *Benzoxazoles* (*n*X-PBO-Y)*: General Procedure. Method A*: Lead(IV) acetate (1.61 mmol) was carefully added in several portions to a soln. of **4** (1.61 mmol) in boiling $CHCl_3$ (40 ml; previously filtered

through activated neutral alumina). The mixture was stirred until a solid residue of lead(II) acetate was formed (30 min). The solid was filtered off, the filtrate concentrated, and EtOH added to precipitate the desired benzoxazole, which was further purified by FC.

Method B: DDQ (12.00 mmol) was added gradually to a soln. of **4** (6.00 mmol) in toluene (200 ml; previously dried over 4 Å molecular sieves) under reflux. The mixture was heated under reflux for 2 h and then allowed to cool down to r.t. Sat. aq. $NaHCO_3$ soln. (200 ml) was added, the mixture extracted with CH_2Cl_2, and the combined org. phase washed with H_2O and dried ($MgSO_4$). The soln. was concentrated, and a large volume of hexane was added to precipitate the desired compound, which was filtered off and purified by FC (silica gel).

Hexyl-2-[4-(Hexyloxy)phenyl]benzoxazole-5-carboxylate (*5HexOOC-PBO-OHex*): By *Method A*: 48% yield. White solid. IR (nujol): 1706, 1610. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.39 (*s*, 1 H); 8.16 (*d*, *J* = 8.8, 2 H); 8.05 (*dd*, *J* = 8.4, 1.2, 1 H); 7.54 (*d*, *J* = 8.6, 1 H); 6.99 (*d*, *J* = 8.8, 2 H); 4.32 (*t*, *J* = 6.6, 2 H); 4.02 (*t*, *J* = 6.6, 2 H); 1.84–1.60 (*m*, 4 H); 1.46–1.31 (*m*, 12 H); 0.89 (*t*, *J* = 6.6, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.4; 164.5; 162.3; 153.5; 142.4; 129.5; 127.2; 126.5; 121.4; 118.0; 114.0; 110.0; 68.0; 65.0; 31.0–14.0. Anal. calc. for $C_{26}H_{33}NO_4$: C 73.73, H 7.8%, N 3.31; found: C 73.26, H 7.59, N 3.31.

2-[4-(Hexyloxy)phenyl]benzoxazole-5-carbonitrile (*5NC-PBO-OHex*): By *Method B*: 87% yield. White solid. IR (nujol): 2221, 1615. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.16 (*d*, *J* = 9.2, 2 H); 7.99 (*s*, 1 H); 7.60 (*m*, 2 H); 7.01 (*d*, *J* = 9, 2 H); 4.03 (*t*, *J* = 6.5, 2 H); 1.83–1.75 (*m*, 2 H); 1.53–1.30 (*m*, 6 H); 0.89 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 162.7; 153.1; 129.9; 128.6; 124.0; 118.9; 118.1; 115.0; 111.5; 108.3; 68.4; 31.5; 29.0; 25.6; 22.5; 14.0. Anal. calc. for $C_{20}H_{20}N_2O_2$: C 74.98, H 6.29, N 8.74; found: C 74.64, H 6.24, N 8.59.

6-(Hexyloxy)-2-[4′-(hexyloxy)phenyl]benzoxazole (*6HexO-PBO-OHex*): By *Method B*: 81% yield. White solid. IR (nujol): 1626. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.10 (*d*, *J* = 8.7, 2 H); 7.56 (*d*, *J* = 8.8, 1 H); 7.06 (*d*, *J* = 2.7, 1 H); 6.98 (*d*, *J* = 8.8, 2 H); 6.90 (*dd*, *J* = 8.7, 2.2, 1 H); 4.03–3.36 (*m*, 4 H); 1.87–1.75 (*m*, 4 H); 1.58–1.23 (*m*, 12 H); 0.92–0.87 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 174.5; 157.4; 151.5; 135.9; 128.9; 119.7; 119.4; 114.7; 112.9; 96.1; 68.8; 68.2; 31.5; 29.2; 25.7; 22.6; 14.0. Anal. calc. for $C_{25}H_{33}NO_3$: C 75.91, H 8.41, N 3.54; found: C 75.98, H 8.45, N 3.41.

4-[6-(Hexyloxy)benzoxazol-2-yl]benzonitrile (*6HexO-PBO-CN*): By *Method B*: 54% yield. White solid. IR (nujol): 2228, 1613. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.28 (*d*, *J* = 7.5, 2 H); 7.77 (*d*, *J* = 7.5, 2 H); 7.64 (*d*, *J* = 8.8, 1 H); 7.09 (*d*, *J* = 2.2, 1 H); 6.97 (*dd*, *J* = 8.2, 2.2, 1 H); 4.00 (*t*, *J* = 6.5, 2 H); 1.86–1.76 (*m*, 2 H); 1.55–1.26 (*m*, 6 H); 0.90 (*t*, *J* = 6.5, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.0; 158.6; 151.9; 135.5; 132.6; 131.3; 127.4; 120.5; 118.3; 114.2; 114.1; 95.9; 68.9; 31.5; 29.1; 25.7; 22.6; 14.0. Anal. calc. for $C_{20}H_{20}N_2O_2$: C 74.98, H 6.29, N 8.74; found: C 74.84, H 6.27, N 8.65.

Hexyl-2-[4-(Hexyloxy)phenyl]benzoxazole-6-carboxylate (*6HexOOC-PBO-OHex*): By *Method A*: 40% yield. White solid. IR (nujol): 1706, 1612. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.20 (*s*, 1 H); 8.17 (*d*, *J* = 8.7, 2 H); 8.05 (*dd*, *J* = 8.3, 1.5, 1 H); 7.71 (*d*, *J* = 8.4, 1 H); 7.00 (*d*, *J* = 8.8, 2 H); 4.33 (*t*, *J* = 6.6, 2 H); 4.02 (*t*, *J* = 6.6, 2 H); 1.82–1.72 (*m*, 4 H); 1.47–1.27 (*m*, 12 H); 0.91–0.86 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.3; 165.7; 162.5; 150.3; 146.2; 129.8; 126.9; 126.2; 118.9; 118.8; 114.9; 111.9; 68.3; 65.4; 31.5; 31.4; 29.1; 28.7; 25.7; 25.6; 22.6; 14.0. Anal. calc. for $C_{26}H_{33}NO_4$: C 73.73, H 7.85, N 3.31; found: C 72.47, H 9.10, N 3.82.

2.5. *2-(4-Phenyl)benzoxazol-5-ols* **7**. *4-Hydroxy-3-nitrophenyl Benzoate* (**5**) was prepared by adapting methods described in [21]: Benzoyl chloride (7 ml) was added dropwise to a soln. of 4-(benzyloxy)-phenol (10.0 g, 0.05 mol) and Et_3N (6.1 g, 0.06 mol) in dry THF at r.t. The mixture was stirred for 30 min, and the resulting precipitate was filtered off. The soln. was washed with sat. aq. Na_2CO_3 soln. (2 × 100 ml) and H_2O (3 × 100 ml), dried ($MgSO_4$), and evaporated: 4-(benzyloxy)phenyl benzoate (13.4 g, 88%). White solid.

$Pd(OH)_2$/C (3.9 g) was gradually added under Ar to a boiling mixture of 4-(benzyloxy)phenyl benzoate (13.0 g, 0.04 mol) in abs. EtOH (170 ml) and cyclohexene (85 ml). The mixture was stirred and heated under reflux for 2 h, allowed to cool down to r.t., and filtered through a pad of *Celite*®. The solvent was evaporated: 4-hydroxyphenyl benzoate (8.5 g, 99%). White solid.

A soln. of 4-hydroxyphenyl benzoate (8.5 g, 0.04 mmol) in CH_2Cl_2 (94 ml) and Et_2O (189 ml) was added to a stirred soln. of $NaNO_3$ (3.4 g, 0.04 mol) in conc. HCl soln. (35.4 ml) and H_2O (47 ml) at r.t. Ac_2O (0.6 ml) was added, and the mixture was stirred for a further 4 h. The aq. phase was extracted

with Et_2O (2×60 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the resulting solid recrystallized from EtOH: 4-hydroxy-3-nitrophenyl benzoate (7.8 g, 76%). Spongy yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.50 (*s*, 1 H); 8.17 (*dd*, *J*=8.4, 1.3, 2 H); 7.99 (*d*, *J*=2.7, 1 H); 7.65 (*m*, 1 H); 7.51 (*dd*, *J*=8.4, 7.5, 2 H); 7.47 (*dd*, *J*=9.0, 2.7, 1 H); 7.21 (*d*, *J*=9.0, 1 H).

2-[4-(Hexyloxy)phenyl]benzoxazol-5-yl Benzoate (**6a**): By *Method A* or *Method B*: 63 or 85% yield, resp. White solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.23 (*d*, *J*=7.6, 2 H); 8.16 (*d*, *J*=8.8, 2 H); 7.64 (*m*, 1 H); 7.49–7.56 (*m*, 4 H); 7.15 (*dd*, *J*=8.6, 2.1, 1 H); 7.01 (*d*, *J*=9.0, 2 H); 4.03 (*t*, *J*=6.4, 2 H); 1.87–1.74 (*m*, 2 H); 1.63–1.25 (*m*, 6 H); 0.90 (*t*, *J*=6.9, 3 H).

2-(4-Cyanophenyl)benzoxazol-5-yl Benzoate (**6b**): By *Method A* or *Method B*: 43 or 77% yield, resp. White solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.34 (*d*, *J*=8.7, 2 H); 8.22 (*d*, *J*=7.1, 2 H); 7.81 (*d*, *J*=8.7, 2 H); 7.65–7.61 (3 H); 7.52 (*m*, 2 H); 7.25 (*dd*, *J*=8.8, 2.4, 1 H).

2-[4-(Methoxycarbonyl)phenyl]benzoxazol-5-yl Benzoate (**6c**): By *Method B*: 89% yield. White solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.34–8.17 (*m*, 6 H); 7.65–7.61 (*m*, 5 H); 7.55–7.50 (*m*, 1 H); 3.95 (*s*, 3 H).

2-[4-(Hexyloxy)phenyl]benzoxazol-5-ol (**7a**): A soln. of KOH (202 mg) in H_2O (5 ml) was added dropwise to a soln. of **6a** (1.5 g, 3.60 mmol) in THF (200 ml) and 96% EtOH (35 ml) at r.t. The mixture was stirred for 2 h, and a large volume of H_2O was added. The resulting mixture was neutralized with AcOH. The THF was evaporated to precipitate the product, which was filtered off and dried at 45° for 48 h under vacuum: **7a** (965 mg, 86%). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.12 (*d*, *J*=8.6, 2 H); 7.35 (*d*, *J*=8.7, 1 H); 7.16 (*d*, *J*=2.4, 1 H); 6.97 (*d*, *J*=9.1, 2 H); 6.82 (*dd*, *J*=8.7, 2.5, 1 H); 6.08–6.04 (*m*, 1 H); 4.01 (*t*, *J*=6.7, 2 H); 1.78 (*m*, 2 H); 1.55–1.23 (*m*, 6 H); 0.89 (*t*, *J*=6.8, 3 H).

4-(5-Hydroxybenzoxazol-2-yl)benzonitrile (**7b**). As described for **7a**, from **6b**: **7b** (93%). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.31 (*d*, *J*=8.4, 2 H); 7.79 (*d*, *J*=8.0, 2 H); 7.45 (*d*, *J*=8.8, 1 H); 7.2 (*d*, *J*=2.6, 1 H); 6.92 (*dd*, *J*=9.3, 2.5, 1 H); 4.92 (*s*, 1 H).

4-(5-Hydroxybenzoxazol-2-yl)benzoic Acid (**7c**). A soln. of KOH (11.88 g) in H_2O (40 ml) was added to a stirred suspension of **6c** (4.20 g, 11.28 mmol) in boiling EtOH (125 ml). After 5 min, H_2O (450 ml) was added and the soln. heated under reflux for 30 min and then allowed to cool down to r.t. The mixture was neutralized with dil. HCl soln., and the solid was filtered off, washed with H_2O and recrystallized from EtOH: **7c** (2.5 g, 87%). White solid. ^{1}H-NMR (300 MHz, (D_6)DMSO): 10.25–9.25 (*s*, 1 H); 8.24 (*d*, *J*=8.4, 2 H); 8.11 (*d*, *J*=8.4, 2 H); 7.57 (*d*, *J*=9.0, 1 H); 7.13 (*d*, *J*=2.4, 1 H); 6.89 (*dd*, *J*=9.0, 2.4, 1 H).

2.6. *5-(Hexyloxy)-2-(4-Y-phenyl)benzoxazoles* (*5HexO-PBO-Y*): *General Procedure.* Hexyl bromide (0.42 ml, 3.01 mmol) was added dropwise under Ar to a mixture of the corresponding **7** (2.73 mmol) and K_2CO_3 (5.46 mmol) in dry dimethylformamide (75 ml). The mixture was heated under reflux for 1 h and then allowed to cool down to r.t. H_2O (120 ml) was added, the mixture extracted with hexane/AcOEt 1:1 (4×100 ml), and the combined org. extract washed with H_2O (3×100 ml), dried ($MgSO_4$), filtered through a pad of silica gel, and evaporated. The crude product was recrystallized from abs. EtOH: 5HexO-PBO-Y, which in some cases was further purified by FC (silica gel, CH_2Cl_2).

5-(Hexyloxy)-2-[4-(hexyloxy)phenyl]benzoxazole (*5HexO-PBO-OHex*): 72% yield. White solid. IR (KBr): 1606. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.12 (*d*, *J*=8.8, 2 H); 7.38 (*d*, *J*=8.8, 1 H); 7.19 (*d*, *J*=2.6, 1 H); 6.98 (*d*, *J*=8.8, 2 H); 6.87 (*dd*, *J*=8.8, 2.6, 1 H); 4.00 (*m*, 4 H); 1.80–1.70 (*m*, 4 H); 1.50–1.21 (*m*, 12 H); 1.01–0.9 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 163.0; 161.0; 156.0; 145.0; 143.0; 129.0; 119.0; 114.0; 113.0; 110.0; 103.0; 68.8; 68.2; 31.6; 31.5; 29.2; 29.1; 25.74; 25.66; 22.6; 22.5; 14.03; 14.01. Anal. calc. for $C_{25}H_{33}NO_3$: C 75.91, H 8.41, N 3.54; found: C 76.23, H 8.49, N 3.55.

4-[5-(Hexyloxy)benzoxazol-2-yl]benzonitrile (*5HexO-PBO-CN*): 170 mg (35%). White solid. IR-(nujol): 2223, 1612. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.29 (*d*, *J*=8.5, 2 H); 7.77 (*d*, *J*=8.7, 2 H); 7.44 (*d*, *J*=8.9, 1 H); 7.22 (*d*, *J*=2.4, 1 H); 6.97 (*dd*, *J*=9.0, 2.5, 1 H); 3.98 (*t*, *J*=6.5, 2 H); 1.84–1.71 (*m*, 2 H); 1.49–1.2 (*m*, 6 H); 0.89 (*t*, *J*=7, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.5; 157.3; 142.7; 132.6; 131.2; 127.8; 118.2; 115.6; 114.5; 110.9; 103.7; 68.9; 31.6; 29.2; 25.7; 22.6; 14.0. Anal. calc. for $C_{20}H_{20}N_2O_2$: C 74.98, H 6.29, N 8.74; found: C 74.76, H 6.38, N 8.59.

Hexyl 4-[5-(Hexyloxy)-2-yl]benzoatebenzoxazole (*5HexO-PBO-COOHex*): 76% yield. White solid. IR (nujol): 1710, 1637. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.27 (*d*, *J*=8.2, 2 H); 8.15 (*d*, *J*=8.2, 2 H); 7.44 (*d*, *J*=8.8, 1 H); 7.23 (*d*, *J*=2.5, 1 H); 6.95 (*dd*, *J*=9.0, 2.4, 1 H); 4.33 (*t*, *J*=6.6, 2 H); 3.99 (*t*, *J*=6.7, 2 H);

1.85–1.71 (*m*, 4 H); 1.5–1.3 (*m*, 10 H); 0.89 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.0; 162.0; 157.0; 145.0; 142.0; 132.0; 131.0; 130.0; 127.0; 115.0; 110.0; 103.0; 68.0; 65.0; 31.0; 29.0; 28.0; 25.0; 22.0; 14.0; 13.0. Anal. calc. for $C_{26}H_{33}NO_4$: C 73.73, H 7.85, N 3.31; found: C 73.28, H 8.03, N 3.73.

3. *Photophysical and Photochemical Investigations.* The photochemical stability of the benzoxazoles was investigated with $CHCl_3$ solns. and with dispersions in solid films of PMMA. Samples were irradiated with a HeCd-laser (*Kimmon Electronics, Ltd.*), providing a power density of 12 mW cm^{-2} for the expanded beam at 325 nm, at different time intervals up to 90 min. Photodegradation of PBOs was followed by UV/VIS spectroscopy and resulted in a decrease in absorbance (*A*). The absorbance at 325 nm was measured before and after every illumination period, and the absorbed energy (*E*) was calculated from the power density of the incident light *P*, the irradiation time *t*, and the mean absorbance A_{mean} (*Eqn. 1*).

$$E = t \cdot P \cdot \left(1 - 10^{-A_{mean}}\right) \tag{1}$$

For comparative purposes, all the nonirradiated samples were prepared to have absorbance 1 at 325 nm to ensure that the same amount of energy was absorbed at the beginning of the irradiation. The photostability of the benzoxazoles was evaluated from the energy required to decrease the absorption at 325 nm to 90% of the initial value; this value is referred as E_{90} and is given in J cm^{-2}. The E_{90} parameter was calculated by plotting the normalized absorbance (A/A_0) *vs.* the absorbed energy (*E*).

Solns. of the benzoxazoles in $CHCl_3$ were placed in a quartz cuvette and exposed to the laser beam. The soln. was stirred with a magnetic bar to guarantee a well-defined dose of optical energy on the whole soln.

Films of benzoxazoles in PMMA were prepared containing 0.1 mol of the benzoxazole/kg of PMMA. Films were deposited onto quartz plates by spin-coating at 2500 r.p.m. for 30 s with a spin-coater (*CT 60* from the *Karl Suess Company*) from a soln. containing 10 μmol of the corresponding dye and 1 ml of PMMA in $CHCl_3$. A PMMA film was used as a reference in the photostability experiments.

4. *Preparation of Oriented Networks and Determination of the Polarized Emission.* Photopolymerizable samples were prepared by dissolving the reactive liquid crystal 4-{{6-[(1-oxoprop-2-enyl)oxy]hexyl}-oxy}benzoic acid 2-methyl-1,4-phenylene ester (C6M supplied by *Philips*), the corresponding 2-phenylbenzoxazole (95 : 5 *w*/*w*), the UV photoinitiator *Irgacure 651* (from *Ciba Spec. Chem.*; 1% weight), and the thermal inhibitor 2,6-di-*tert*-butylphenol (200 ppm) in CH_2Cl_2. The solvent was evaporated at r.t., and the residual solvent was removed under vacuum. Inspection of the blends by optical microscopy indicated good miscibility of the components. Photopolymerization was carried out in cells for planar alignment (5-μm thickness; from *Linkam*), and these were filled by capillary action. The oriented films were produced at the nematic phase temp. (between 90 and 100°) under illumination with 365-nm light (*PL-S 9W/10-Philips* lamp) for 15 min. The material C6M has a nematic phase between 86 and 116°, and shows a maximum absorbance at 268 nm without emission.

Polarized luminescence measurements were recorded by means of a *Perkin-Elmer LS50B* spectrofluorimeter with a sample holder designed to measure liquid-crystal cells [7]. The measurements were taken with the excitation beam polarized in parallel to the rubbing direction of the cell and the detection polarizer either parallel or perpendicular. Therefore, the emission intensity at the maximum of the emission band in the rubbing direction ($I_{\parallel}$) and perpendicular ($I_{\perp}$) to it were determined and corrected for the dichroic response of the equipment. The emission dichroic ratio (R_{em}) was calculated as the quotient of these two values.

REFERENCES

[1] S. M. Kelly, 'Flat Panel Displays. Advanced Organic Materials', The Royal Society of Chemistry, Cambridge, 2000.
[2] C. Weder, C. Sarwa, A. Montali, C. Bastiaansen, P. Smith, *Science (Washington, D.C.)* **1998**, *279*, 835.
[3] M. Grell, D. D. C. Bradley, *Adv. Mater.* **1999**, *11*, 895.
[4] D. J. Broer, in 'Radiation Curing in Polymer Science, Polymerization Mechanisms', Vol. III, Eds. J. P. Fouassier and J. F. Rabek, Elsevier Science, London, 1993, p. 383.

[5] A. P. Davey, R. G. Howard, W. J. Blau, *J. Mater. Chem.* **1997**, *7*, 417.
[6] C. Sanchez, R. Alcala, R. Cases, L. Oriol, M. Pinol, *J. Appl. Phys.* **2000**, *88*, 7124.
[7] C. Sanchez, B. Villacampa, R. Cases, R. Alcala, C. Martinez, L. Oriol, M. Pinol, *J. Appl. Phys.* **2000**, *87*, 274.
[8] A. E. A. Contoret, S. R. Farrar, M. O'Neill, J. E. Nicholls, G. J. Richards, S. M. Kelly, A. W. Hall, *Chem. Mater.* **2002**, *14*, 1477.
[9] B. M. Krasovitskii, B. M. Bolotin, 'Organic Luminescent Materials', VCH, Weinheim, 1988.
[10] Y. Kanagae, K. Peariso, P. P. Martinez, *Appl. Spectrosc.* **1996**, *50*, 316.
[11] J.-M. Kim, T.-E. Chang, J.-H. Kang, K. H. Park, D.-K. Han, K.-D. Ahn, *Angew. Chem., Int. Ed.* **2000**, *39*, 1780.
[12] J.-M. Kim, B.-O. Chong, K. H. Park, T.-E. Chang, D. K. Han, D. J. Choo, K.-D. Ahn, *Polym. Bull.* **2000**, *44*, 79.
[13] C. W. Ko, Y. T. Tao, A. Danel, L. Krezeminska, P. Tomasik, *Chem. Mater.* **2001**, *13*, 2441.
[14] C. H. Chen, J. Shi, C. W. Tang, *Macromol. Symp.* **1997**, *125*, 1.
[15] R. Centore, S. Concilio, B. Panunzi, A. Sirigu, N. Tirelli, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 603.
[16] P. Ambrosiano, R. Centore, S. Concilio, B. Panunzi, A. Sirigu, N. Tirelli, *Polymer* **1999**, *40*, 4923.
[17] K. H. Park, K. M. Yeon, M. Y. Lee, S.-D. Lee, D.-H. Shin, C. J. Lee, N. Kim, *Polymer* **1998**, *39*, 7061.
[18] S. Kim, S. Y. Park, *Macromolecules* **2001**, *34*, 3947.
[19] K. H. Park, M. G. Kwak, W. S. Jahng, C. J. Lee, N. Kim, *React. Funct. Polym.* **1999**, *40*, 41.
[20] S. Kim, J. Sohn, S. Y. Park, *Bull. Korean Chem. Soc.* **1999**, *20*, 473.
[21] U. Caruso, R. Centore, A. Roviello, A. Sirigu, *Macromolecules* **1992**, *25*, 2290.
[22] V. Vill, 'LiqCryst Database' edn. 4.3, LCI Publisher GmbH, Hamburg, 2002.
[23] A. I. Pavluchenko, N. I. Smirnova, V. V. Titov, E. I. Kovshev, K. M. Djumaev, *Mol. Cryst. Liq. Cryst.* **1976**, *37*, 35.
[24] S. Kim, S. Y. Park, *Mol. Cryst. Liq. Cryst.* **1999**, *337*, 405.
[25] R. Centore, B. Panunzi, A. Roviello, A. Sirigu, P. Villano, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *334*, 3203.
[26] A. Reiser, L. J. Leyshon, D. Saunders, M. V. Mijovic, A. Brigth, J. Bogie, *J. Am. Chem. Soc.* **1972**, *94*, 2414.
[27] J. Catalán, E. Mena, F. Fabero, F. Amat-Guerri, *J. Chem. Phys.* **1992**, *96*, 2005.
[28] J. K. Dey, S. K. Dogra, *Indian J. Chem., Sect. A* **1990**, *29*, 1153.
[29] J. K. Dey, S. K. Dogra, *Can. J. Chem.* **1991**, *69*, 1539.
[30] G. F. Woolfe, M. Melzig, S. Schneider, F. Dörr, *Chem. Phys.* **1983**, 213.

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