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Ionic liquid crystals bearing bipyridinium and pentaphenylene groups

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1. Introduction

The driving forces leading to a liquid-crystalline behavior are the mutual repulsive interactions (dispersive forces) between the different parts of molecules [1] and if one of these parts is an ionic group it will play a key role in the structure stabilization, particularly in lamellar mesophases [2-4]. Ionic liquid crystals show unique characteristics that can be different from those of conventional or neutral liquid crystals. For instance, a tendency to form a spontaneous homeotropic phase has been reported to occur particularly in ionic liquid crystals, such as the N. N-dialkyl-substituted diazoniabicyclooctane [5] and some alkylammonium derivatives [6]. This property is useful for the surface treatment of substrates that may allow the deposition of functional thin films with highly ordered molecules [7]. In this work we are interested in liquid crystals bearing *p*-phenylene groups, which are usually modified with alkyl chains to render them soluble, facilitating in this way their processing [8]. Recently, this kind of π -conjugated groups has aroused a huge interest because of their luminescent properties in the blue region [9–12]. In a previous work, dialkyloxy-substituted oligophenylenes were functionalized at one chain end with bromine to obtain intermediates [13], which were further used to quaternize the pyridine [14]. The resulting pyridinium salts developed a mesomorphic behavior of the

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ABSTRACT

Molecular and polymeric liquid crystals bearing bipyridinium and pentaphenylene groups were synthesized and characterized. These new ionic liquid crystals develop single layer smectic-type mesophases with molecules tilted or orthogonal with respect to the smectic planes as a function of temperature. A high tendency to develop a homeotropic behavior was observed for the molecular liquid crystals. A molecular arrangement was proposed in which the different parts of molecules are fully segregated from one another with the ionic groups stabilizing the smectic order. These molecules show a luminescence in the blue region that combined with the liquid–crystalline behavior could be interesting for the fabrication of light emitting thin films with ordered molecular emitters. © 2010 Elsevier B.V. All rights reserved.

smectic type in a wide temperature range (110-210 °C). By X-ray diffraction analysis it was found that the different parts of molecules (oligophenylene core, alkyloxy chains and pyridinium ring associated with its counterion) segregate from one another in layered domains periodically arranged in space, as it normally occurs for amphiphilic molecules. These dialkyloxy-substituted oligophenylenes can be also functionalized at both chain ends with bromine to obtain intermediates that can be reacted with bipyridine (viologen) to produce molecular and polymeric ionic liquid crystals. These ionic molecules are interesting not only because they develop both liquid-crystalline and light emission properties, but also because they show a tendency to develop a homeotropic phase when they are deposited onto a glass substrate. There are few reports on liquid crystals bearing a viologen or bipyridyl group [15], and we thought it of interest to combine this bifunctional group with a rigid π -conjugated core to investigate the thermotropic behavior as well as the light emission characteristics of the resulting ionic molecules. So, in the present work, the mesomorphic behavior and the light emission characteristics of new ionic liquid crystals bearing both bipyridinium and pentaphenylene groups are described and discussed.

2. Experimental

2.1. Materials

1-bromobutane, 1,10-dibromodecane, 1,12-dibromododecane, 4,4'bipyridyl, butyllithium 1.6 M in hexanes, 4'-bromo-(1,1'-biphenyl)-4-ol, triisopropyl borate, bromine (Br₂), calcium chloride, potassium carbonate, sodium carbonate, hydrochloric acid, hydroquinone, sodium hydroxide, potassium iodide, calcium sulfate di-hydrated, tetrakis

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(triphenylphosphine)palladium(0), ethyl acetate, acetone, chloroform, methylene chloride, dimethylformamide (DMF), ethanol, ethyl ether, hexane, methanol, carbon tetrachloride, tetrahydrofuran (THF) and toluene were purchased from Aldrich Co. and/or J. T. Baker, and were used as received unless otherwise specified. The 4,4'-bipyridyl was recrystallized from toluene. Calcium sulfate di-hydrated was dehydrated at 250 °C for 8 h. DMF was dried with anhydrous calcium sulfate for 72 h and distilled at 80 °C under reduced pressure. THF was distilled from a sodium/benzophenone complex before used.

2.2. Synthesis

lonic molecules were synthesized following the reaction route outlined in Scheme 1. The 1, 4-bis($4'(\omega$ -bromoalkyloxy)biphenyl)-2,5-dibutoxybenzene (IV or V) was synthesized through the Suzuki cross-coupling reaction between the 1,4-dibutoxy-2,5-phenylbisboronic acid (I) and the $4'(\omega$ -bromoalkyloxy)-4-bromobiphenyl (II or III) using Pd[0] as catalyst [16,17]. The chemical precursors I–III were synthesized according to procedures described in detail in previous works [18]. The dibromo end-functionalized molecules (IV and V) were then reacted with 4,4'-bipyridine to obtain two molecules having at both chain ends a mono-substituted bipyridinium group (M-10 and M-12) and a polymer bearing both bipyridinium and pentaphenylene groups linked through flexible spacers (P-10). The procedures for obtaining the intermediates (IV and V) and final molecules (M-10, M-12 and P-10) are described in the next paragraphs.

2.2.1. 1,4-bis(4'-(ω -bromoalkyloxybiphenyl)-2,5-dibutoxybenzene (IV and V)

In a 250 mL two-neck round bottom flask equipped with condenser, magnetic stirring and an inner gas inlet (argon), 1 g (3.2 mmol) of I, 2.98 g (6.4 mmol) of II or 3.2 g (6.4 mmol) of III, 50 mL of toluene, 0.11 g of $[P(C_6H_5)_3]_4Pd(0)$ and 19.4 mL of an aqueous solution of Na₂CO₃ 2 M, were introduced. The solution was degassed, vigorously stirred and heated up to 100 °C for 24 h. After cooling to room temperature, the

solution was transferred to a 500 mL separation funnel to be washed with distilled water. The organic phase was transferred to a round bottom flask to eliminate the solvent by evaporation under reduced pressure. Finally, the intermediate IV (or V) was purified by chromatographic column using CHCl₃ as solvent and elusion medium. Compounds IV and V were recuperated as white powders. Yields around 70% were obtained for both IV and V. m.p. 132 °C (IV) and 110 °C (V). ¹H NMR (CDCl₃) δ (ppm) = 7.65 (*m*, 12H, Ar), 7.05 (*d*,*s*, 6H, Ar), 4.0 (*m*, 8H, CH₂ α -O), 3.4 (*t*, 4H, CH₂ α -Br), 1.85 (*m*, 8H, CH₂ β -O), 1.75 (*m*, 4H, CH₂ β -Br), 1.2-1.6 (*m*, 28H IV or 36H V, -CH₂-) and 0.92 (*t*, 6H, CH₃). Elemental analysis (%): IV (C₅₈H₇₆Br₂O₄) calcd C 69.87, H 7.68; found C 70.19, H 7.43 and V (C₆₂H₈₄Br₂O₄) calcd C 70.71, H 8.04; found C 69.68, H 8.26.

2.2.2. 1,4-bis- $[(4'-(\omega-(bipyridinium bromide)alquiloxy)biphenyl]$ -2,5-butoxybenzene (M-10 and M-12)

In a 50 mL pear-shaped Schlenk flask 0.2 g (0.2 mmol) of IV or 0.2 g (0.19 mmol) of V, 0.156 g (1.0 mmol) of 4, 4'-bipyridine and 15 mL of DMF, were introduced. Then, the solution was degassed, stirred and heated up to 100 °C for 8 days. After cooling to room temperature, the solution was poured drop wise into 150 mL of ethyl acetate to obtain a precipitate that was recuperated by filtration and dried in a vacuum oven at 30 °C for 24 h. The recuperated compound (M-10 or M-12) is a beige colored solid. Yields for both reactions were higher than 90%. ¹H NMR (CDCl₃/MeOD) δ (ppm) = 9.2 (*d*, 4H, bpy), 8.8 (*d*, 4H, bpy), 8.3 (*d*, 4H, bpy), 7.7 (d, 4H, bpy), 7.5–7.7 (m, 12H, Ar), 6.9–7.1 (d, s, 6H, Ar), 4.8 (*t*, 4H, CH₂α-N), 3.9–4.1 (*m*, 8H, CH₂α-O), 2.0 (*m*, 4H, CH₂β-N), 1.6–1.8 (*m*, 8H, –CH₂β-O), 1.1–1.5 (*m*, 28H M-10 or 36H M-12, –CH₂–), and 0.9 (*t*, 6H, CH₃). Elemental analysis (%): M-10 (C₇₈H₉₂Br₂N₄O₄ · 1H₂O) calcd C 70.57, H 7.13, N 4.22; found C 68.91, H 7.48, N 3.9 and M-12 (C₈₂H₁₀₀Br₂N₄O₄·1H₂O) calcd C 71.18, H 7.43, N 4.05; found C 68.66, H 7.91, N 3.70. Half molecule of water was considered per pyridiniumbromine ion pair, although it seems that more than half molecule of water was absorbed by each one of them. The ¹H NMR spectrum of these compounds showed a singlet at 2.45 ppm that was attributed to water. This signal frequently appears in pyridinium salts, even for those dried



Scheme 1. Reactions involved in the preparation of ionic liquid crystals bearing bipyridinium and pentaphenylene groups. (i) Toluene, Pd[0] and Na₂CO₃/H₂O; (ii) DMF, 4,4'-bipyridine and (iii) DMF and IV (or V).

at 80 °C under reduced pressure overnight [4,19]. The bound water is then difficult to remove as deduced from both the 1 H NMR spectra and the elemental analysis results.

2.2.3. Polymer bearing bipyridinium and pentaphenylene groups (P-10)

In a 50 mL pear-shaped Schlenk flask 0.059 g (0.059 mmol) of IV, 0.078 g (0.059 mmol) of M-10 and 15 mL of DMF, were introduced. Then, the solution was degassed, stirred (magnetic bar) and heated up to 100 °C for 8 days. After cooling to room temperature, the solution was poured drop wise into 150 mL of ethyl acetate to obtain a precipitate that was recuperated by filtration and dried in a vacuum oven at 30 °C for 24 h. The recuperated compound (P-10) is a brown colored solid. ¹H NMR (CDCl₃/MeOD) δ (ppm) = 9.2 (4H, bpy + 2H, end-bpy), 9.0 (4H, bpy), 8.8 (2H, end-bpy), 8.3 (2H, end-bpy), 7.75 (2H, end-bpy), 7.4-7.65 (12H, Ar), 6.8-7.1 (6H, Ar), 4.6-4.8 (4H, CH₂ α -N), 3.8-4.0 (8H, CH₂ α -O), 2 (4H, -CH₂ β -N), 1.5-1.8 (8H, -CH₂ β -O), 1.2-1.5 (28H, -CH₂-), and 0.92 (6H, CH₃).

2.3. Characterization

The chemical structure of molecules was verified by ¹H NMR spectroscopy using a Jeol spectrometer (300 MHz) and CDCl₃, THF-d or CDCl₃/CD₃OD as solvents. Elemental analysis was performed in a Carbo Erba (1106) instrument at the Charles Sadron Institute, Strasbourg France. The thermal stability of compounds was determined on vacuum dried samples and using a TGA 951 thermal analyzer from DuPont Instruments connected to a nitrogen vector gas and heating at 10 °C min⁻¹ from room temperature to 800 °C. The DSC traces were obtained in a differential scanning calorimeter (MDSC 2920) from TA Instruments at heating and cooling rates of 5 °C min⁻¹. Optical textures of mesophases were registered upon cooling (2 °C/min) in an Olympus BH-2 polarizing optical microscope coupled with a Mettler FP82HT hot stage. The structure of mesophases was obtained at different temperatures by means of X-ray diffraction analyses using an INEL CPS120 diffractometer ($K_{\alpha 1}$ copper radiation and a home-made electrical oven). The UV-visible absorption spectra were recorded on a Shimadzu 2401 PC spectrophotometer with a detection interval of 190-800 nm, while the emission spectra were obtained using a Perkin Elmer LS 50B spectrofluorimeter illuminating the samples with a UV light of $\gamma = 10$ nm higher than the $\gamma_{abs.max}$. Solutions for optical analyzes were prepared in spectroscopic grade chloroform at concentrations of 0.04 mg mL $^{-1}$.

3. Results and discussion

3.1. Synthesis

Several reaction steps were considered to obtain the intermediates IV and V as well as the molecules bearing both pyridinium and pentaphenylene groups (M-10, M-12 and P-10). The intermediates were synthesized through procedures described in previous papers [18], so here the discussion is focused only on the molecules bearing pyridinium and pentaphenylene groups. These ionic molecules were synthesized through a quaternization reaction conducted in a high dielectric constant solvent (DMF). The mono-quaternization of the bipyridine proceeds relatively fast, however the quaternization of the second nitrogen atom of the bipyridine is much more difficult because it becomes less electropositive. This effect, associated with the poor solubility of the growing molecules, may be the cause of the limitations in molecular weight as deduced from the ¹H NMR of the polymer P-10. The chemical structure of M-10 and M-12 was confirmed from the ¹H NMR spectra, which were detailed in the experimental section. The ¹H NMR signals of the bipyridnium moiety are located at low fields (from δ = 7.7 to 9.2 ppm) as it is shown in Fig. 1a for the compound M-10. For the molecules bearing mono-substituted bipyridines four signals ($\delta = 9.2, 8.8, 8.3$ and 7.7 ppm) can be distinguished in the ¹H NMR spectrum; additionally, two complex signals ($\delta = 6.9$ and 7.5 ppm) corresponding to protons of the pentaphenylene group can be appreciated close to this region. For the polymer P-10 the ¹H NMR spectrum (Fig. 1b) shows signals of both mono- and disubstituted bipyridine moieties, along with those corresponding to the pentaphenylene groups. The signals of protons of the mono-substituted bipyridines (chain ends) are located at $\delta = 9.2, 8.8, 8.3$ and 7.7 ppm, while those (only two signals) corresponding to the di-substituted bipyridine appear at $\delta = 9.0$ and 9.2 ppm. From these signals it was calculated that the resulting molecule contains around 5 repeating units, which seems to be guite small for a polymer; however, the repeating unit by itself is guite long in such a way that the resulting molecule can be considered as a low molecular weight polymer (\sim 5800 g mol⁻¹). It should be mentioned that, during the quaternization reactions (conducted under vacuum), solutions turned out colored from yellow to deep blue, though such color vanished progressively after the reaction flasks were opened and the solutions entered in contact with air. Purified salts (M-10 and M-12) were yellowish powders and filtrates were rather colorless. The polymer P-10 remained brown colored even after purification. Colored reaction solutions have been previously observed in guaternization reactions of polymers bearing pyridine rings [20]. Such color was attributed to the formation of ion pairs that give rise to charge-transfer bands, as it was long time ago proposed by Boucher and Mollet for polymers bearing pyridinium groups [21]. It is to point out that several experiments were conducted to obtain the polymer P-12, however in any of them a polymer was obtained, even for long reaction times.

3.2. Mesomorphic behavior

The intermediates IV and V were first studied by DSC and their corresponding thermograms (Fig. 2) showed a monotropic transition. By optical microscopy a *Schlieren* texture was observed in both compounds indicating without ambiguity the presence of a nematic phase (Fig. 3).

The molecules bearing mono-quaternized bipyridines (M-10 and M-12) were analyzed by thermogravimetry exhibiting an initial decomposition temperature of around 200 °C, which was considered as the maximum temperature for the thermotropic examination. This relatively low decomposition temperature is without doubt associated to the poor thermal stability of the CH_2-N^+ bond of pyridinium salts [22]. The DSC traces of these compounds showed one or two endotherms/exotherms as it can be appreciated in Fig. 4. On heating from room temperature the M-10 compound showed only one small endotherm centered around 100 °C and upon cooling it showed a broad exotherm that extends from 185 to 140 °C. On the other hand, optical textures were registered upon cooling



Fig. 1. Low field of the ¹H NMR spectra of M-10 (a) and P-10 (b). Solvent: CDCl₃/MeOD.





Fig. 3. Optical textures of IV (left) and V (right).

and for this compound a homeotropic behavior (Fig. 5) was observed in the all temperature range. In fact, the reduced number of batonnets appearing on cooling (around 184 °C) from the isotropic state vanished progressively as the temperature decreased, and the image became dark



Fig. 4. Heating (\rightarrow) and cooling (\leftarrow) DSC thermograms of M-10, M-12 and P-10.

and remained as it is up to room temperature. This phenomenon has been frequently observed in rodlike molecules bearing quaternary ammonium end groups, which adhere to the surface of the glass substrate with molecules pointing out in a perpendicular direction with respect to the substrate plane [7]. The DCS traces of the M-12 compound exhibited two endotherms on heating from room temperature, one of them centered at 100 °C and the other localized between 160 and 175 °C; however, on cooling from the isotropic state only a broad exotherm was appreciated at high temperature. It is to point out that the optical textures of M-12 showed batonnets upon cooling (around 175 °C), that also disappear leading to a homeotropic texture, but in this case a transition leading to a non-specific birefringent texture (Fig. 5) was observed around 100 °C. By DSC it was difficult to detect something in this region (according to Fig. 4), even though by polarizing optical microscopy (POM) and X-ray diffraction a clear transition was observed around 100 °C. For the polymer P-10, a transition was observed by DSC on heating around 110 °C, although by POM it was pretty difficult to locate such transition. Due to discrepancies observed between DSC and POM experiments, a detailed structural analysis as a function of temperature was performed by X-ray diffraction, in both heating and cooling modes.

3.3. Structural characterization

The X-ray diffraction patterns of M-10 and M-12 were obtained at different temperatures (upon heating and cooling) and results are shown in Figs. 6 and 7. In order to avoid a thermal degradation of compounds, a maximum temperature of 190 °C was used in these measurements. It can be noticed that the X-ray diffraction patterns show in general two equidistant Bragg reflections (d_{001} and d_{002}), revealing the layered structure, typical of a smectic-type mesophase [23]. For the M-10 compound (Fig. 6) such diffraction peaks are suddenly shifted



Fig. 5. Optical textures of M-10, M12 and P-10.



Fig. 6. Low angles region of the X-ray diffraction patterns for the compound M-10. Registered upon heating and cooling at different temperatures.



Fig. 7. Low angles region of the X-ray diffraction patterns for compound M-12. Registered upon heating and cooling at different temperatures.



Fig. 8. Smectic period (d_{001}) as a function of temperature for compounds M-10 and M-12.

towards low angles (on heating around 100 °C), indicating a change in the layer spacing (d_{001}) from 37.5 to 54.5 Å. By plotting d_{001} as a function of temperature (Fig. 8) it can be clearly seen that, upon heating, a firstorder transition occurs leading to an expansion in the layer spacing of approximately 17 Å. In contrast, on cooling from 190 to 50 °C the layer spacing remains relatively constant meaning that the same or almost the same molecular arrangement is maintained in all this temperature range. This behavior seems to be consistent with the optical observations, where the homeotropic texture remained unaffected from 184 °C to room temperature. On the other hand, the X-ray diffraction patterns of M-12 revealed a structural transition in both heating and cooling experiments (Fig. 7). Upon heating d_{001} suddenly changes (around 100 °C) from 39 to 56.8 Å, indicating an expansion of the layer spacing of 17.2 Å (Fig. 8), which is of the same order to that observed for M-10. Upon cooling the layer spacing decreases abruptly (around 100 °C) and attains in a reversible way a value of 39 Å. This reversible change coincides well with the optical observations, where it was detected that, upon cooling, the homeotropic texture turned out birefringent near 100 °C.

The smectic phases were definitely characterized by the shape of the scattering signal in the wide angles region of the X-ray patterns (not shown here). Upon heating, the M-10 and M-12 compounds showed, below 100 °C, a single sharp peak, indicating a hexatic order, and above 100 °C, a broad peak typical of a liquid-like order [23]. Upon cooling, the M-10 compound showed only a broad peak in the all temperature range indicating that there is no order of the molecules within the smectic layers. In a different way, the M-12 compound developed (upon

cooling) a broad peak above 100 °C and a single sharp peak below 100 °C. In order to determine the molecular arrangement of M-10 and M-12 in the mesophase, the measured layer spacing was compared with the length of the molecule in its most extended conformation (L=54and 59 Å for M-10 and M-12, respectively), calculated by using molecular modeling software (Spartan'04). The d_{001}/L radios shown in Table 1 indicate that the molecular arrangement corresponds to a single-layered smectic-type mesophase with molecules orthogonal (high temperature) or tilted (low temperature) with respect to the smectic planes, as it is schematically represented in Fig. 9. In this model the different parts of molecules are fully segregated from one another and periodically arranged in space. Within the ionic sublayers the cations and anions are facing each other; they may be also facing the opposite charge ions of the neighboring smectic layers, stabilizing in this way the mesophase [4,24]. This model is plausible because both the π - π interactions of the long pentaphenylene groups and the interaction of the electrical charges of the ionic groups (pyridinium rings and counter ions) seem to be well satisfied. Similar molecular arrangements were recently proposed for related molecules possessing both pyridinium and terphenylene groups [14].

Compared to the M-10 and M-12 compounds, the X-ray diffraction patterns of the polymer P-10 did not exhibit abrupt changes in the position of the Bragg diffraction peaks, but a rather continuous and reversible shift as it is observed in Fig. 10. By plotting d_{001} against temperature (Fig. 11) it can be seen that the layer spacing of the polymer P-10 expands only 7 Å. The d_{001}/L radios found for the polymer also correspond to a tilted (at low temperature) or to an orthogonal (at high temperature) single-layered smectic-type mesophase, although in this case the molecules are progressively tilted attaining an angle smaller than that calculated for the small molecules (Table 1). In the wide angles region of the X-ray diffraction patterns of the polymer (not shown here) only a broad diffraction peak was appreciated in the all temperature range, indicating that there is no order of molecules within the smectic layers. A molecular arrangement proposed for the polymer P-10 is schematically represented in Fig. 12. In this molecular arrangement the repeating units may be covalently connected from one smectic layer to the other. According to all these observations, the types of mesophases presented by M-10, M-12 and P-10 can be assigned as described in Table 1.

The models proposed in this work for the molecular and polymeric liquid crystals are some similar to that proposed for Ohta et al. [5] for ionic liquid crystals based on N, N-dialkyl-substituted diazoniabicyclooctanes, which show a spontaneous homeotropic alignment and that seem to be stabilized by the ionic groups, as it is proposed in the present work.

The phase transition between orthogonal and tilted smectic phases can be either first or second-order. First-order transitions are those characterized by a discontinuous change in the tilt angle of molecules with respect to the smectic plane, while second-order transitions are those showing a continuous or smooth change in such tilt angle [25]. In a firstorder transition two distinct phases coexist at the transition temperature [23]. For the M-10 and M-12 compounds, the first-order transition was determined from the sudden shift in the position of the low angles X-ray diffraction peaks, occurring around 100 °C in both compounds (Figs. 6 and 7). Moreover, the presence of diffraction peaks of two distinct phases in the same X-ray diffraction pattern (Fig. 7, 100 °C upon heating) demonstrates that the phase transition is of first-order; this evidence

Table 1		
Structural data for M-10, M-12 and P-10. Minimum ((*) and maximum	(**) attained values.

		, , ,		
Compound	L, Å	d_{001} Å	Mesophase	Tilt angle, °
M-10	53.4	54.5**	HexF/I \rightarrow (100 °C) SmA \rightarrow (185 °C) I	SmA~0
		37.5*	Remains homeotropic \leftarrow SmA (185 °C) \leftarrow I	HexF/I = 45.4
M-12	58.5	56.8**	HexF/I \rightarrow (100 °C) SmA \rightarrow (175 °C) I	SmA = 13.8
		39.0*	HexF/I (100 °C) \leftarrow SmA (175 °C) \leftarrow I	HexF/I = 48.0
P-10	47.0	46.9**	SmC (80° \leftrightarrow 120 °C) SmA \rightarrow (190 °C) I	SmA = 3.7
		40.1*	SmC (80° ↔ 120 °C) SmA ← (190 °C) I	SmC = 31.4



Fig. 9. Schematic representation of the molecular arrangement (one layer) for compounds M-10 and M-12 in the mesophase.

indicates that both the orthogonal and the tilted mesophases coexist at the transition region. Similar results were reported by Ratna et al. [26] for the coexistence of an orthogonal and a tilted mesophase observed in a very narrow temperature region (<1 °C) for the 4-(3-methyl-chloropentanoy-loxy)-4'-heptyloxybiphenyl, although in such a case it corresponds to a first-order SmA–SmC* phase transition. In the case of the polymer P-10, the reversible second-order phase transition was attested by the continuous shift of diffraction peaks as a function of temperature.

The driving forces leading to a smectic order are the mutual interactions between the different chemical groups of molecules. From the models (Figs. 9 and 12) it is clear that the smectic layer formation is primarily due to the strong interactions between the cations and anions, which are stronger than the π - π and the van der Waals interactions of pentaphenylenes and alkyl chains, respectively. Nevertheless, the pentaphenylenes and alky chains are long enough to segregate in separate sublayers. In rodlike liquid crystals it is quite common to observe a thermotropic sequence involving orthogonal and tilted mesophases in which the phase transition is first-order, as for instance for the reversible first-order HexB-HexF transition observed in an enaminoketone derivative series [25]. Our experimental data is quite limited to make a full discussion about the possible driving forces that induce the first-order transition in the M-10 and M-12 compounds, however in a first approximation we believe that it could be associated to the melting process of the alkoxy chains, particularly to the melting of the butoxy groups substituted in the central ring of pentaphenylenes. On a heating run, these groups melt in a short temperature interval, becoming flexible enough to reduce in some extent the packing constrains; in this case the rodlike molecules can adopt an orthogonal arrangement. Inversely, in a cooling run the flexible groups become stiff and probably more unfolded; in this case the packing constrains will induce the tilt of molecules. The molecular origin of tilt in smectic liquid crystals has been extensively reviewed in theoretical and experimental studies and it was frequently attributed to the structural constrains and specific interactions produced by the lateral chemical groups substituted in rodlike molecules [27]. No matter what the constrains are, the observed significant expansion of the layer spacing (around 17 Å) gives a clear idea of the importance of the packing constrains that are relieved at the phase transition observed in the M-10 and M-12 compounds. For the long polymeric molecules (P-10), which are located in several contiguous smectic layers, the second-order phase transition should be related to this and some other structural constrains.

3.4. Absorption and emission properties

The absorption and emission spectra were obtained from spectroscopic grade chloroform solutions of M-10, M-12 and P-10 (Fig. 13). The absorption spectra showed two peaks centered at 260 and 345 nm for the compounds M-10 and M-12, and 285 and 345 nm for the Polymer P-10. The emission spectra showed only one maximum centered approximately at 400 nm for the three compounds. It can be noticed that both absorption and emission peaks are well separated from one another (Stokes shift) in a way they overlap only in a quite narrow region of the spectrum. The large Stokes shift indicates that the ground and excited states are different and probably associated to the torsion of



Fig. 10. Low angles region of the X-ray diffraction patterns for compound P-10 registered upon heating and cooling at different temperatures.



Fig. 11. Smectic period (d_{001}) as a function of temperature for the polymer P-10.



Fig. 12. Schematic representation of the molecular arrangement (one layer) of the polymer P-10 in the mesophase.

adjacent phenylene rings due to excitation [12]. The fact that there is almost no difference in the wavelengths obtained for compounds M-10 and M-12 confirms that the alky spacers have no effect on the conjugation [18]. Finally, no differences were found between the characteristics of the emitted light between small molecules (M-10 and M-12) and the polymer (P-10); the emission process is associated solely to the electronic excited states occurring in the pentaphenylene core, which in all molecules is well separated from the bipyridinium groups through flexible spacers.



Fig. 13. UV-vis absorption (solid line) and emission (dashed line) spectra obtained from solutions of M-10 (a), M-12 (b) and P-10 (c). Solvent: $CHCl_3$.

4. Conclusion

New molecular and polymeric liquid crystals bearing bipyridinium and pentaphenylene groups were synthesized and characterized. They develop single-layered smectic-type mesophases with molecules tilted (low temperature) or orthogonal (high temperature) with respect to the smectic planes. A high tendency to develop a homeotropic phase was observed for the molecular liquid crystals. A molecular stacking model was proposed in which the different parts of molecules are fully segregated from one another and periodically arranged in space; the ionic sublayers facing each other in neighboring smectic layers contribute to stabilize the smectic order. This model is plausible because the π - π interactions of the pentaphenylene groups and the interactions of the electrical charges of ionic groups are satisfied. These molecules showed a light emission centered at around 400 nm that combined with a liquid-crystalline behavior may be interesting for the preparation of organic active layers having molecular light emitters aligned in a preferential direction.

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