

Synthesis and blue luminescence of a soluble newly designed carbazole main-chain polymer

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

A new electroactive polymer with alternating conjugated–nonconjugated repeating units in the main chain was synthesized by step growth polymerization of α,ω -bis(*N*-carbazolyl)octane in chloroform solution with excess of iron trichloride, and in the presence of *N*-ethylcarbazole as a terminating agent. The resulting α,ω -*N*-ethylcarbazole terminated poly(3,3'-bicarbazyl-*N,N'*-octylene)s are readily soluble in common organic solvents and have good film-forming capabilities, partly because of the special design of the polymer backbone constituted by stiff bicarbazyl chromophores linked by flexible eight-carbon segments. Soluble materials with molecular weights up to 105 g/mol and polydispersity indices around 3.3 were obtained. Purified samples exhibiting quite low polydispersity indices (in the range 1.5–1.7) can be prepared by a selective fractionation of the crude polymer from benzene/methanol mixtures. Structural analysis of these new 'stairs-like' polymers disclosed their well-defined character with an aromatic linkage exclusively at position 3 on the carbazole moieties. Electrochemical studies of polymer films exhibited two reversible redox processes between 0 and 1.5 V vs saturated calomel electrode. The photoluminescence (PL) of the polymer in solution and as cast films revealed an intense blue emission and the same intensity level than that of the *N,N'*-diethyl-3,3'-bicarbazyl molecule, taken as a model of the aromatic segment of the repeating unit. Such a processable and purifiable polymer with bicarbazyl-isolated fluorophores is quite promising for the fabrication of efficient blue light-emitting devices. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbazoles; Blue luminescence; carbazole

1. Introduction

Over the past decade, electroactive and photoactive polymers have gained much more importance because of the versatility of applications they afford. For instance, such polymers (and related oligomers) have been utilized in the fabrication of light-emitting devices [1–8],¹ electrochromic displays [9–11], laser dyes [12,13], and organic transistors [14,15]. Polymeric materials for optoelectronics offer considerable processing advantages over small molecule systems since (i) polymer films can be generated from solution deposition techniques, e.g. by spin-coating, (ii) they are usually glassy, and (iii) they have good mechan-

ical properties at room temperature. However, the main drawback encountered so far with polymers in optoelectronic devices such as LEDs has been their operational stability, which is largely connected with their chemical purity. Indeed, polymerization products are usually polluted by impurities such as catalyst residues that cannot be separated by distillation or sublimation. Therefore, the impurity trap charge carriers lead to a decrease in the device efficiency and shortening of its lifetime.

Furthermore, among the three basic colors required for multicolor displays, i.e. red, green, and blue, many efforts have been devoted to obtain blue-light emitting polymeric materials since the blue luminescence is difficult to achieve with inorganic materials. A high value of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy band-gap is required for blue light emission. Various approaches have been used to obtain such macromolecular materials, such as the use of oligomers with

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¹ Reviews on the chemistry of electroluminescent polymers are given in Refs. [6–8].

high-energy gap and that of copolymers with short conjugated segments.² Oligomers usually exhibit a poor film-forming ability and a high tendency for crystallization. Copolymers containing short segments of poly(*p*-phenylenevinyls) (PPVs), poly(*p*-phenylenes) (PPPs), poly(alkylfluorenes), or poly(oxadiazoles) have been obtained by introducing bulky substituents in the main chain [17–22]. Another strategy has been adopted by synthesizing polymers composed of short conjugated segments interconnected by solubilizing nonconjugated spacers [23–28]. Such materials are expected to retain the electronic properties of the conjugated oligomer blocks and to possess the processability and long-term morphological stability of the higher molecular weight polymers.

We have previously shown that the chemical oxidation of *N*-alkylcarbazoles by iron trichloride (FeCl₃) exclusively and quantitatively yields the dimer, i.e. 3,3'-bicarbazyl [29]. Moreover, we have recently reported that single-layer organic light-emitting diodes (OLEDs) based on the *N,N'*-diethyl-3,3'-bicarbazyl with indium tin oxide (ITO) and Mg(Ag) electrodes, show a violet-blue electroluminescence (sharp peak centered at $\lambda \approx 415$ nm) with an external quantum efficiency of about 0.1% [30,31]. However, it must be pointed out that these OLEDs showed a low stability that has been attributed to morphological changes of the carbazolic emission layer. Indeed, thin films based on bicarbazyl dimeric species tend to show dendrites on defect locations after a few days in air, which affects both the homogeneity of the film and the performance of the device. As these dendrites grow up, the blue light emission decreases and finally leads to the diode breakdown. In order to overcome this drawback, our group started investigating few years ago the possibility of incorporating bicarbazyl dimeric moieties along macromolecular chains while keeping their electroactive properties [32,33]. We now report the synthesis, characterization, and purification of poly(3,3'-bicarbazyl-*N,N'*-octylene), a polymer in which stiff bicarbazyl chromophores are separated by flexible octylene segments and wherein the *N,N'* catenation of the carbazole subunits was expected to retain the electroactivity of the 3,3'-bicarbazyl repeat units. Furthermore, both the physico-chemical and the photoluminescence (PL) properties of this 'stair-like' main-chain polymer are presented and compared with those of the bicarbazyl molecule in order to evaluate the magnitude of the polymer effect.

2. Experimental

2.1. Materials

Carbazole (Aldrich) was recrystallized from hexane and obtained as slightly brownish needles. 1,8-Dibromooctane (Aldrich) was distilled over calcium hydride (CaH₂) under

vacuum and kept under argon atmosphere. *N*-ethylcarbazole (Aldrich) was recrystallized from ethanol and obtained as white needles. Chloroform and toluene were freshly distilled prior to utilization. Iron trichloride (Aldrich) was used as received. All other reagents, e.g. sodium hydroxide (NaOH) pellets and triethylbenzylammonium chloride (TEBAC) were purchased from Aldrich and used without further purification. All reactions were carried out under argon atmosphere.

2.2. Preparation of the monomer 1

Compound **1** was prepared according to the method reported by Sasabe et al. [34]. ¹H NMR (CDCl₃, 200 MHz, δ ppm): 8.1 (d, H_{4,5}, 4H), 7.34–7.45 (m, H_{2,3,6,7}, 8H), 7.17–7.25 (m, H_{1,8}, 4H), 4.23 (t, >N-CH₂-, 4H), 1.8 (unresolved m, >N-CH₂-CH₂-, 4H), 1.25 (unresolved m, >N-(CH₂)₂-CH₂-CH₂-, 8H). ¹³C NMR (CDCl₃, 50 MHz, δ ppm): 140.4 (C_{8a,9a}), 125.5 (C_{3,6}), 122.7 (C_{4a,4b}), 120.3 (C_{4,5}), 118.6 (C_{2,7}), 108.6 (C_{1,8}), 42.9 (>N-CH₂-), 29.1 (>N-(CH₂)₃-CH₂-), 28.8 (>N-CH₂-CH₂-), 27.1 (>N-(CH₂)₂-CH₂-).

2.3. Preparation of the polymer 2

A solution of 2 g (4.5 mmol) of **1** and 439 mg (2.25 mmol) of *N*-ethylcarbazole in 200 ml of freshly distilled chloroform was poured into a 500 ml three-necked flask fitted with a reflux condenser and an argon inlet. 6.57 g (40.5 mmol) of iron(III) chloride were then quickly added. The mixture was vigorously stirred at room temperature for 4 h. The resulting greenish solution was poured into a large excess of acidic water (HCl: 0.01 M) and washed several times with the same low concentration solution. The brownish organic layer was then washed with distilled water, dried over Na₂SO₄, filtered, and concentrated. The residue was precipitated twice from methanol to give a white precipitate. After filtration, and drying in a vacuum oven, we obtained the poly(3,3'-bicarbazyl-*N,N'*-octylene) **2** in quantitative yield as a white powder. The fractionation of the polymer **2** was carried out by adding methanol to the polymer solution (10%, w/v) in benzene at room temperature. It was performed in three steps. The efficiency of the fractionation was checked by size exclusion chromatography (SEC). ¹H NMR (CDCl₃, 200 MHz, δ ppm): 8.36 (s, H₄), 8.09–8.13 (d, H₅), 7.71–7.74 (d, H₂), 7.2–7.35 (unresolved m, H_{7,8}), 7.17 (unresolved m, H₁), 4.17 (unresolved m, >N-CH₂-), 1.78 (unresolved m, >N-CH₂-CH₂-), 1.23 (unresolved m, >N-(CH₂)₂-CH₂-CH₂-). ¹³C NMR (CDCl₃, 50 MHz, δ ppm): 141.1 (C_{9a,9a'}), 140.6 (C_{9a''}), 139.7 (C_{8a,8a'}), 139.2 (C_{8a''}), 133.5 (C_{3,3'}), 125.6 (C_{2,2',6,6'}), 123.6 (C_{4b,4b'}), 123.3 (C_{4a,4a'}), 120.5 (C_{5,5'}), 118.9 (C_{4,4',7,7'}), 108.9 (C_{1,1',8,8'}), 43.2 (>N-CH₂-), 37.6 (>N-CH₂-CH₃), 29.1 (>N-(CH₂)₃-CH₂-), 28.9 (>N-CH₂-CH₂-), 27.1 (>N-(CH₂)₂-CH₂-), 13.7 (>N-CH₂-CH₃).

² A review on blue light-emitting polymers is given in Ref. [16].

2.4. Characterization

^1H and ^{13}C NMR spectra were recorded in solution in CDCl_3 with a Bruker AC200 spectrometer at 200 and 50 MHz, respectively, all chemical shifts (δ in ppm) were measured relative to tetramethylsilane (TMS) or to the solvent.

The molecular weight and the molecular weight distribution were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF), using a Waters apparatus (pump 6000A, differential refractometer detector R401) equipped with five μ -styragel columns (10^5 , 10^4 , 10^3 , 500, 100 Å) calibrated with polystyrene standards.

Differential scanning calorimetry (DSC) was conducted on powder specimens with a Perkin–Elmer DSC System 4 in flowing nitrogen. Calibration was made with indium ($T_m = 156.6^\circ\text{C}$ and $\Delta H_m = 28.4\text{ J g}^{-1}$). Glass transition temperatures were recorded at the half-height of the corresponding heat capacity jumps. A heating rate of $20^\circ\text{C min}^{-1}$ was used.

Electrochemical studies were performed with a Solea-Tacussel apparatus (PJT 35-2 potentiostat, GSTP 4 generator). Typical cyclic voltammetry (CV) experiments of solution-cast films of **2** onto conducting support were carried out in acetonitrile (HPLC grade, Fisher Scientific) containing 0.3 M of LiClO_4 (Acros) as supporting electrolyte in a one-compartment cell equipped with three electrodes. The working anode (support for films of **2**) was glassy carbon (surface area 7 mm^2), the counter-electrode, a platinum wire ($1.2\text{ cm}/0.38\text{ cm}^2$), the reference electrode being a saturated calomel electrode (SCE).

UV–visible spectroscopy was carried out using a Perkin Elmer spectrometer (model Lambda 12) in the range 190–1100 nm (resolution 1 nm). We measured the optical density of the samples in a freshly distilled THF solution ($\approx 5 \times 10^{-4}\text{ M}$) in a quartz UV cell ($l = 5 \times 10^{-2}\text{ cm}$).

We have recorded the luminescence of the polymer **2**, either solvated in a freshly distilled THF solution ($\approx 10^{-4}\text{ M}$) using a UV quartz cell (1 cm^2) or in amorphous state (thickness of the films was around $5\text{ }\mu\text{m}$; they were prepared from THF solution onto a quartz plate). In both cases, the samples were irradiated at 313 nm with a KDP (potassium diphosphate) doubled dye laser light, pumped by the second harmonic of a pulsed Nd:YAG laser. The experimental setup has been previously described [35]. Photoluminescence (PL) of the samples is collected by a one-meter quartz fiber fitted on the entrance slit of a Spex monochromator ($f = 270\text{ mm}$, 150 l/mm) and is analyzed with the help of an intensified charge coupled device array detector (OMA, model 1460, EGG PARC). Spectra, obtained for different positions and inclinations of the collecting fiber with respect to the specular reflection of the exciting light beam, are accumulated during a few milliseconds.

3. Results and discussion

3.1. Synthesis and characterization of carbazole main-chain polymers

In a first step, we synthesized monomer 1,8-bis(*N*-carbazolyl)octane **1** based on two carbazole moieties linked via the nitrogen atoms according to the method described by Sasabe et al. [34].

In a second step, we attempted to polymerize **1** similar to the method we have previously described for the dimerization of *N*-alkylcarbazoles, i.e. by oxidative coupling by FeCl_3 in chloroform solution [29]. We obtained materials insoluble in traditional organic solvents, at room temperature and we did not attempt any further, a solubilization in more drastic conditions. We adopted two strategies to overcome this insolubility. We tried first to change the structure of the spacer separating the carbazole groups. With some efforts, we isolated more or less soluble materials, which is not described here [36]. A less tedious and more efficient method that held our attention is the shortening of the macromolecular chain length by adding to the reaction medium, *N*-ethylcarbazole (EtCz) as a monofunctional-terminating agent. Fig. 1 shows the polymerizing system constituted by **1**/ FeCl_3 /EtCz. In such conditions, as expected, the ‘poly-dimerization’ of **1** by FeCl_3 , gives rise to the formation of soluble polymeric materials, namely α,ω -*N*-ethylcarbazole terminated poly(3,3′-bicarbazyl-*N,N'*-octylene) **2**.

We found that a **1** to EtCz molar ratio equal to 0.5 was the most appropriate to get wholly soluble polymer samples with molar masses as high as 105 g/mol. Since the polymer backbone is constituted of successive kinks (‘stairs’) introduced by the *N,N'* catenation between the carbazole subunits and separated by flexible octylene spacers and hence creating a disturbance of its rigid nature, i.e. a decrease of both the chain symmetry and the intermolecular interactions of aromatic units, materials exhibit a particularly good solubility in common organic solvents such as THF and CHCl_3 .

The step growth polymerization character of the coupling reaction of **1** shows up in the size exclusion chromatography (SEC) of the crude material **2** (see Supporting Information

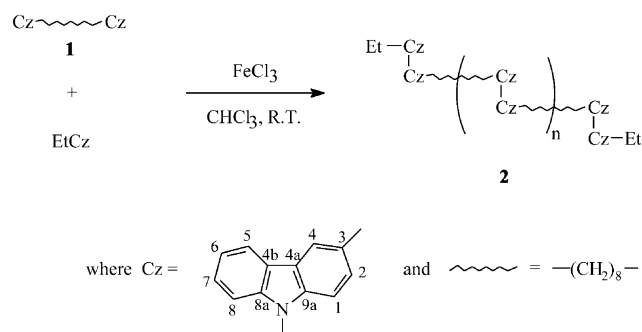


Fig. 1. Synthesis of *N*-ethylcarbazole terminated poly(3,3′-bicarbazyl-*N,N'*-octylene) **2**.

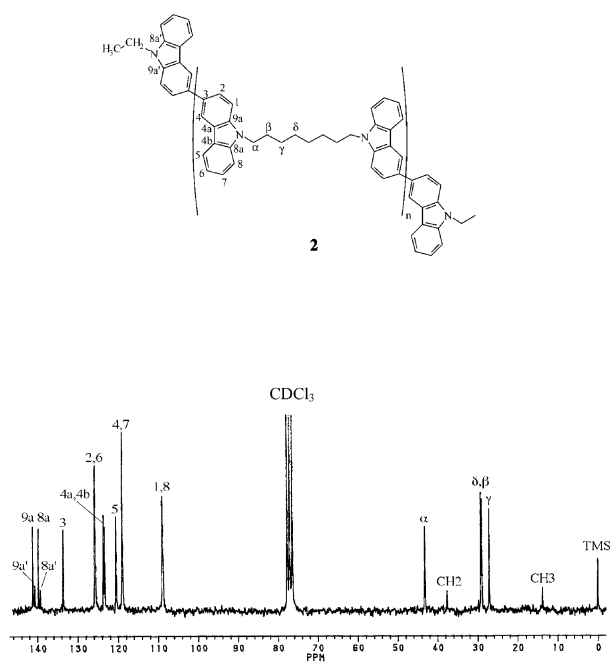


Fig. 2. ^{13}C NMR spectrum of fractionated *N*-ethylcarbazole terminated poly(3,3'-bicarbazyl-*N,N'*-octylene).

trace (a)). Multimodal chromatograms were obtained, corresponding to the different chain lengths with degrees of polymerization up to 60 and a polydispersity index $I_p = \bar{M}_w/\bar{M}_n$ of 3.2. The lowest molar mass signal observed is related to the dimer $(\text{EtCz})_2$, which resulted from the oxidative homocoupling of the terminating agent EtCz (5% yield in the optimum conditions where $[\mathbf{1}]/[\text{EtCz}] = 0.5$). With the aim to investigate the luminescence properties of these polymers based on bicarbazyl, and knowing from previous studies [30,31] that the presence on $(\text{EtCz})_2$ dimer or other impurities like some FeCl_3 left are harmful for this kind of investigation, we performed fractional precipitations of the crude materials. Fractionation setup consisted in successive precipitations of polymer populations from a benzene solution of the parent polymer (10%, w/v) by addition of a miscible nonsolvent such as methanol. Following this procedure, the highest molar mass polymer chains precipitate first. Since the samples used for these fractionation experiments were polydispersed and composed of distinct species, it was possible to achieve a quite efficient separation according to the heterogeneity of the molar mass distribution. This method of fractionation was found appropriate in our case since we were able to isolate several pure fractions of well-defined 'poly(bicarbazyl)' in the range of molar masses 6000–20 000 g/mol and with low polydispersity indices ($I_p \sim 1.5$ – 1.7) (see Supporting Information traces (b), (c), and (d)). It is noteworthy that upon fractionation, no trace of impurity or undesired dimer $(\text{EtCz})_2$ was detected.

The purity and the structure of **2** were confirmed from ^1H and ^{13}C NMR spectra. For instance, the ^{13}C NMR spectrum

(Fig. 2) shows the characteristic signals associated with the resonance of the carbon atoms of the bicarbazyl moieties according to the literature values [37] and confirms the molecular structure. In particular the quaternary carbons of the 3,3' linkage were easily assigned at 133.5 ppm. We saw no evidence for the formation of other bicarbazyl attachment. The high regioselectivity of the FeCl_3 -catalyzed polycondensation process of **1** can be explained by comparison with what have been described for the oxidative dimerization of *N*-substituted carbazoles [29,38]. Indeed it has been shown that the 3 and 6 positions of the radical-cations generated by oxidation are extremely reactive. Two of these react rapidly via coupling-deprotonation at the 3 position to yield 3,3'-bicarbazyls. The oxidative coupling of **1** by FeCl_3 is quantitative and this system is very 'clean' when compared with the nonselective condensation obtained with fluorene and thiophene [6–8]. Furthermore, the signature of the termination reaction by cross coupling between a macromolecular radical-cation and a *N*-ethylcarbazolylium shows up in the ^{13}C NMR of the low molar mass fraction, as typical signals at $\delta = 37.8$ ppm ($>\text{N}-\text{CH}_2-\text{CH}_3$) and 13.8 ppm ($>\text{N}-\text{CH}_2-\text{CH}_3$), respectively.

Polymer **2** was also investigated using differential scanning calorimetry (DSC). Parent polymer only showed a glass transition at 151 °C. This is consistent with the assumption of amorphous homogeneous materials. These results can be compared with those obtained for poly(*N*-octyl-3,6-carbazolylenes) [39], polymers with an all-carbazole skeleton and with octyl pendant groups. The highest molar mass materials (104 g/mol) exhibited a lower glass transition at 70 °C and a melting temperature at 153 °C indicating a semi-crystalline nature. That appears as an evidence of the effect of the disturbance of the rigid-rod nature of the backbone by introducing kinks and/or flexible segments in the main-chain. As a result, polymers become soluble in more common solvents and it should be noted that highly transparent homogeneous films of polymer **2** could be obtained by casting from CHCl_3 or THF solutions.

Even though the macromolecular and structural features described above confirmed the well-defined character of the poly(bicarbazyl-octylene), it was of a paramount importance to perform further characterizations in order to determine their electroactivity, due to the presence of bicarbazyl chromophores along the polymethylene chain. First of all, we studied by cyclic voltammetry the electrochemical behavior of polymer films casted from parent solution in THF onto glassy carbon electrodes (in 0.3 M $\text{LiClO}_4/\text{acetonitrile}$ solution with a Pt counter-electrode). Cyclic voltammograms (Fig. 3) exhibited two redox couples with oxidation peaks at 0.88 and 1.16 V/SCE, i.e. at 5.72 and 6.00 V/vacuum, respectively. (The conversion from the electrochemical axis to the vacuum scale has been done assuming the normal hydrogen electrode NHE to be at 4.6 eV versus vacuum [40] and taking into account the potential difference of +0.24 V between SCE and NHE.) The two electrochemical redox processes are diffusion-controlled (charge

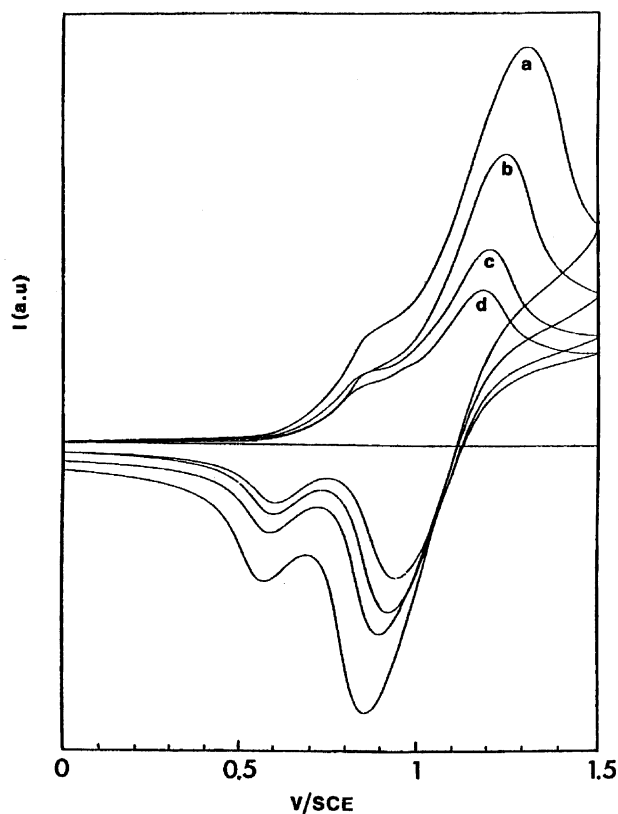


Fig. 3. Cyclic voltammograms of polymer films cast onto a glassy carbon microelectrode as a function of scan rates: (a) 0.02 V/s; (b) 0.01 V/s; (c) 0.005 V/s; (d) 0.003 V/s.

transport and counterions migration) as found in the direct proportionality of peak anodic and of peak cathodic currents with the square root of the scan rate, i.e. $I_{a,c} = f(v^{1/2})$ linear, according to the Randles–Sevcik equation [41]. Such an electrochemical behavior is typical of the bicarbazyls [38,42]. The two anodic waves correspond to the formation of the bicarbazolylium radical-cations for the first step followed by their oxidation into dication through the second step. The reasons for which the two waves involve such different currents remain unclear. That could be attributed to oxidation of the terminal groups and then of the main chain groups but also to the difference between the charge transport resistances of the film with the two considered potential domains (high resistance in the insulating neutral state between 0 and 0.8 V and a lower resistance in the conducting doped state above 0.8 V). Utilization of a transparent indium tin oxide (ITO) glass electrode allowed us to observe the color changes associated with the two-oxidation processes. Polymer films display two color transitions upon electrochemical oxidation in the range 0–1.5 V/SCE, i.e. from colorless to green and from green to blue. Similar electrochromic effects have been observed by spectroelectrochemistry in the case of poly(*N*-butyl-3,6-carbazolylenes) [43], and have been ascribed to the formation of radical cations (green

species) followed by their oxidation into dication (blue species).

Finally, it is noteworthy that bicarbazolylium radical-cations can easily be obtained by a simple chemical oxidation of polymer samples by iron(III) chloride in chloroform solution. Optical spectra of the yielded dark-green solutions exhibited a typical broad absorption band with a maximum centered at 825 nm and an intensity remaining unchanged after several days under nitrogen, thus disclosing the remarkable stability of the oxidized species.

3.2. Optical properties

These new ‘polybicarbazyl’ derivatives have been synthesized for their potentially interesting luminescent properties. Indeed, we have recently shown that the photo- and electroluminescence of the *N,N'*-diethyl-3,3'-bicarbazyl is characterized by an intense emission with a maximum at ≈ 415 nm with a full width at half-maximum of ≈ 50 nm [30,31]. Single-layer diodes based on this compound exhibited a well-defined blue light, a good luminance (20 Cd/m²) at relatively low operating current density (250 A/m²) and an external quantum efficiency of about 0.1%. In a first step, we found interesting to compare the spectroscopic properties of our synthesized polymer **2** containing isolated bicarbazyl fluorophores in the main chain with those of the (EtCz)₂ dimer molecule. The comparison of the absorption spectra obtained in THF solutions shows a noticeable similarity, demonstrating that the bicarbazyl core is the absorbing entity (Fig. 4). Spectra display strong absorption peaks at 244 and 304 nm, and bands of lower intensities at longer wavelengths around 345 and 357 nm. All these absorption bands are characteristic of the dimer structure [30,31]. They are themselves red-shifted (≈ 12 nm for the lowest $S_1 \leftarrow S_0$ transition) and broadened compared to the absorption bands of the EtCz monomer [44].

The photoluminescence (PL) features of (EtCz)₂ molecules and of **2**, irradiated with a UV laser light at

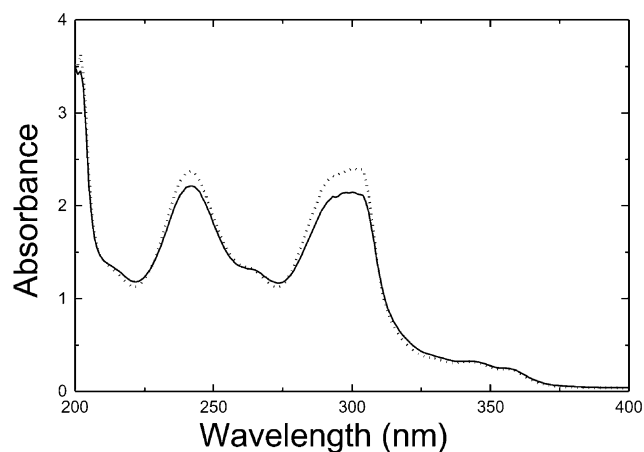


Fig. 4. Comparison of UV-visible spectra of carbazole dimer (EtCz)₂ (---) and bicarbazyl-based polymer **2** (—) in THF solution (quartz cell), 7×10^{-4} and 5×10^{-4} M, respectively.

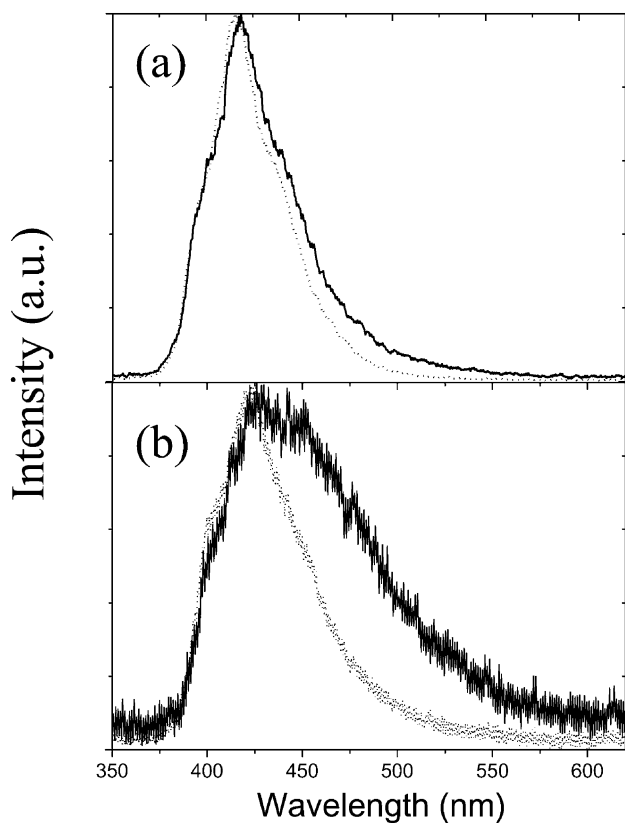


Fig. 5. Normalized photoluminescence spectra ($\lambda_{\text{excitation}} \approx 313$ nm) of *N,N'*-diethyl-3,3'-bicarbazyl (---) and of poly(*N,N'*-octylene-3,3'-bicarbazyl) **2** (—) both as solutions (a) and as cast films (b).

313 nm, were studied in THF solutions or as films deposited onto quartz plates. An intense blue luminescence peaking at 417 nm was observed both for the (EtCz)₂ dimer and the polymer in THF solution. As shown in Fig. 5(a), the normalized fluorescence spectra are similar, thus indicating that in such conditions, the polymer retains the fluorescence property of the bicarbazyl core. From these results it can be deduced that no interaction occurs in the excited states, between chromophores belonging to the same macromolecular chain or to a neighboring one. The photoluminescence of solutions exhibited a remarkable stability since no degradation was noticed even after several hours upon laser irradiation. Furthermore, a few changes are denoted when comparing the luminescence spectra obtained in solution and in the solid state. The spectra obtained with the films (Fig. 5(b)) are of a lower intensity, broadened and also red-shifted compared to the solution spectra. Because the solvent (THF) used for the film preparation readily evaporates, it is possible that some different morphological forms are responsible for the red shoulder observed in the spectra of the polymer film. In fact, molecular aggregates present in the film might be responsible for this specific broadening [45]. However, it is noteworthy that the emission intensity of the polymer layer is of the same order of magnitude than that of the dimer. Whence, it

could be concluded that the octylene segments of the macromolecular chains play a neutral role with respect to excitons, the confinement of which is not altered. A supporting argument is found in the PL of the poly(*N*-trioxadecyl-3,6-carbazolyene) [46], an all-carbazole polymer. Indeed, although the carbazole units are linked in the polymer backbone the PL has a maximum at 440 nm and a quantum yield of 20%. These spectroscopic comparisons demonstrate the interest of our polymer as a new electroactive material. In particular, the 'polydimer' presents the advantages, over the dimer molecule, of better film-forming ability, processing and orientation possibilities that might be exploited to increase the luminescence quantum efficiency.

4. Conclusion

The step growth polymerization of α,ω -bis-(*N*-carbazolyl)octane **1** by oxidative coupling by FeCl₃ yielded new 'polybicarbazyls', i.e. poly(3,3'-bicarbazyl-*N,N'*-octylenes) **2**. We showed the importance of using a 'terminating agent', i.e. an *N*-ethyl-carbazole, in such a 'multidimerization' process as an efficient means to reduce the chain length and to obtain readily soluble materials of relatively high molar masses. We were able to 'purify' these latter by a selective fractionation and thus obtained 'impurity-free' polymer samples of various molar masses with low polydispersity indices. Structural analysis of **2** disclosed its well-defined character and the high regioselectivity of the step growth polymerization process. The electrochemical oxidation of polymer films disclosed two electrochemical redox processes associated with two color changes: colorless–green and green–blue successively. The photoluminescence (PL) of the polymer in solutions and as cast films revealed an intense and well-defined blue light emission of the same intensity level than that of the *N,N'*-diethyl-3,3'-bicarbazyl molecule. Finally, the 'polybicarbazyl' derivatives investigated in this study exhibit strong fluorescence in the blue region (emission maximum around 417 nm) both as solutions and as cast films. This interesting photophysical property makes therefore, these easily processable materials quite promising for applications in blue-light-emitting devices.

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