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Synthesis and Characterization of New Electroluminescent Material Based on Carbazole, and Terphenyle

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Abstract: Conjugated polymers containing carbazole moieties either in the main or side chains have attracted much attention because of their unique electronic properties, their high photoluminescence quantum efficiency, and thermal stability. In this paper we present a combined experimental study of the structure, optical and spectroscopic properties of a new copolymer based on carbazole and terphenyl (PEcbz-Ter). This copolymer was prepared by oxidative copolymerization. First, we describe the route for preparing the new copolymer. Then, we report characterization measurements based on solid state Nuclear Magnetic Resonance (¹³C NMR), IR absorption, UV-visible absorption, photoluminescence spectroscopy, and X-ray diffraction. We report also additional transient photoluminescence (PL) study on this copolymer in order to complete a broader comparative view of optical properties of these two systems and particularly, to investigate the nature of the excited states, their lifetime and decay processes. We also determined the Quantum Yield (QY) of the PL emission for the copolymer. The decay behaviors provide an understanding on how the conformational changes and the chemical nature of the substituent groups can tune the emission properties in such structures and change their QY.

Keywords: PEcbz-Ter; UV-Vis-NIR absorption; ¹³C RMN; PL; PLRT; and X-ray diffraction.

I. INTRODUCTION

Recently, more attention has been focused on the organic conducting polymers. Due to their specific properties; these compounds are widely used for opto-electronic device applications, such as organic light emitting diodes (OLEDs) [1-2], field-effect transistors [3-5] (OTFTs), photovoltaic cells [6-8], portable electronic [9], lasers [10-11]. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. Polymers with a low band gap are desired in optoelectronic applications such as LEDs or solar cells [12].

In recent years, several studies reported on the synthesis of some blend materials based on poly (N-vinylcarbazole) PVK [13-15]. These materials form a subset of the organic materials under study for blue EL applications [16-19]. In fact PVK absorbs entirely in the UV region and as a consequence of its photoconductivity, its wide band gap. One of the most important conjugated polymers which allow a very flexible structure and promising properties are copolymers which contain both carbazole and derivatives (Fig. 1) and p-terphenyl (Fig. 2) units. This material have proved to be of interest in combining the properties associated with the two different conjugated rings [20] and have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency, and thermal stability. This family of materials can be prepared by electrochemical or chemical polymerization [21-22]. The necessity of finding new organic materials has caused great concern in scientific community, in this regard. In order to

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understand well the optical and electronic properties and hence the improvement of such devices in which conjugated polymers are used as active layers, IR spectra can provide structural information. On the other hand, photoluminescence can often be greatly enhanced by increasing the intrinsic stiffness of a polymer backbone or by inducing large bulky side groups to weaken intermolecular interactions. The emission spectrum of a conjugated polymer depends basically on its π - π^* band gap, which can be tailored using different structures [23]. In this paper we present a combined experimental study of the structure, optical and spectroscopic properties of a new copolymer based on carbazole and terphenyl (PEcbz-Ter). This copolymer was prepared by oxidative copolymerization. First, we describe the route for preparing the new copolymer. Then, we report characterization measurements based on solid state Nuclear Magnetic Resonance (^{13}C NMR), IR absorption, UV-visible absorption, photoluminescence spectroscopy, and X-ray diffraction. We report also additional transient photoluminescence (PL) study on this copolymer in order to complete a broader comparative view of optical properties of these two systems and particularly, to investigate the nature of the excited states, their lifetime and decay processes. We also determined the Quantum Yield (QY) of the PL emission for the copolymer.

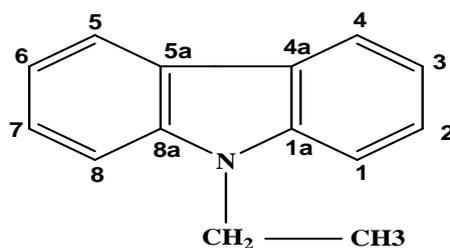


Fig. 1: The chemical structure of Poly (9-Ethylcarbazole) (PEcbz).

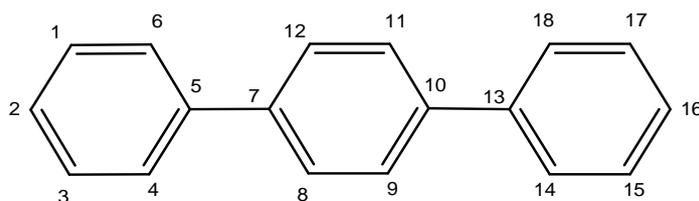


Fig. 2: The chemical structure of p-terphenyl (Ter).

II. EXPERIMENTAL METHODS

Poly(9-Ethylcarbazole) (PEcbz) powder (97%), p-Terphenyl (Ter) (99%), ferrichloride (FeCl_3), chloroform CHCl_3 (99%), methanol CHOH (99,9%), used for the synthesis of the studied compounds were purchased from Aldrich chemistry, A Fisher Scientific International and Riedel-deHaën and were purified before use by usual procedures. In this work, the copolymer (PEcbz-Ter) is dissolved and oxidatively polymerized with FeCl_3 . The solvent was Chloroform (HPLC grade). The microanalysis measurements were carried out with X-ray diffraction studies on a Philips PW1800 diffractometer equipped with a curved detector ($K\alpha$ ray of copper $\lambda=1,5418 \text{ \AA}$). Infrared spectra were obtained with a Brüker Vector 22 Fourier transform spectrophotometer. Samples were prepared in pellets of KBr mixed with the organic compound under study. NMR spectra were acquired at room temperature (RT) using a Brüker Avance 500MHz spectrometer operating at 125.7 MHz for ^{13}C , using a 4-mm double bearing Brüker probehead. All rotors were spun under a dry nitrogen flow. Spectra were referenced to tetramethylsilane (TMS) for ^{13}C (using adamantane as a secondary reference). NMR spectra were acquired using a ramp-amplitude sequence [24], a 2 ms contact time, a

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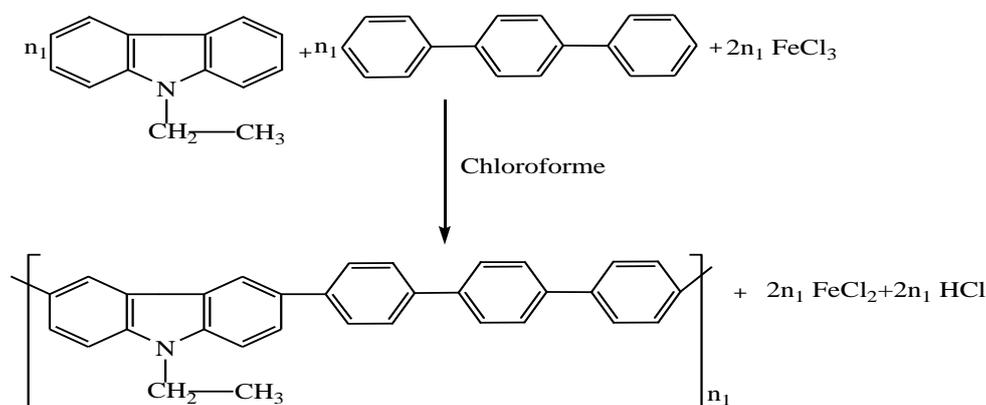
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repetition time of 2 s and a 15 kHz MAS spinning rate. 1H decoupling during acquisition was achieved using the TPPM method [25] with a radiofrequency (RF) field of approximately 60 kHz. Continuous-wave (cw) photoluminescence (PL) measurements were collected on a Jobin-Yvon Fluorolog 3 spectrometer using a Xenon lamp (500W) at room temperature. To make paper easy to read, we recall briefly the ultrafast time resolved photoluminescence experiments which were carried out with the regenerative amplified femtosecond laser system installed in University of Nantes. This setup delivers 100 pulses at 1 kHz, 800 nm, and 1 W. Samples were excited at wavelength $\lambda_{exc} = 400$ nm. The time-resolved emission spectra were spatio-temporally detected with a high dynamic range Hamamatsu C7700 streak camera of temporal resolution <20 ps.

III. SYNTHESIS PROCEDURE OF THE COPOLYMER PECBZ-TER

The polymerization was been developed by a single procedure to prepare a mixture of Ecbz with terphenyl (scheme 1). The procedure adopted was to cross link PEcbz by reacting CHCl_3 solution of Ecbz with anhydrous FeCl_3 and to add a known amount of p-terphenyl with undergo polymerization, and the resulting PTER would subsequently participate in copolymer formation process. The detail of PEcbz-Ter preparation are as follows: 2 g of poly(9-Ethylcarbazole) was dissolved in approximately 100 ml of CHCl_3 , and 4.8 g of anhydrous FeCl_3 dispersed in 50 ml of CHCl_3 were successively added to the dispersion under stirring. The colour of the solution changed from colourless to dark green, suggesting the oxidation of PEcbz and its cross-linking. Then 2.3g of p- terphenyl were added to the mixture. The system was kept under stirring at room temperature for 3 days. Then, an excess of methanol (600–800 ml) was added to the solution for 12 h to remove residual FeCl_3 . The solution was filtered and about 3.6 g of a green mass was collected and kept firstly under pressure for 30 min then under vacuum at 80°C for 48 h. A dark green powder was obtained in the fully oxidative (doped) state.



Scheme 1: Synthesis of the PECbz-Ter.

For a better understanding of the relationship between the copolymers structure and their vibrational or optical properties, we discuss in the following section infrared absorption, UV–Vis absorption and PL emission results.

IV. RESULT AND DISCUSSION

A. Infrared results

Fig. 3 displays experimental normalized optical infrared spectrum of the PECbz-Ter powder in the range of $400\text{--}1750\text{ cm}^{-1}$. First of all, we note that qualitatively the fine structure is a signature of high organized copolymer structure.

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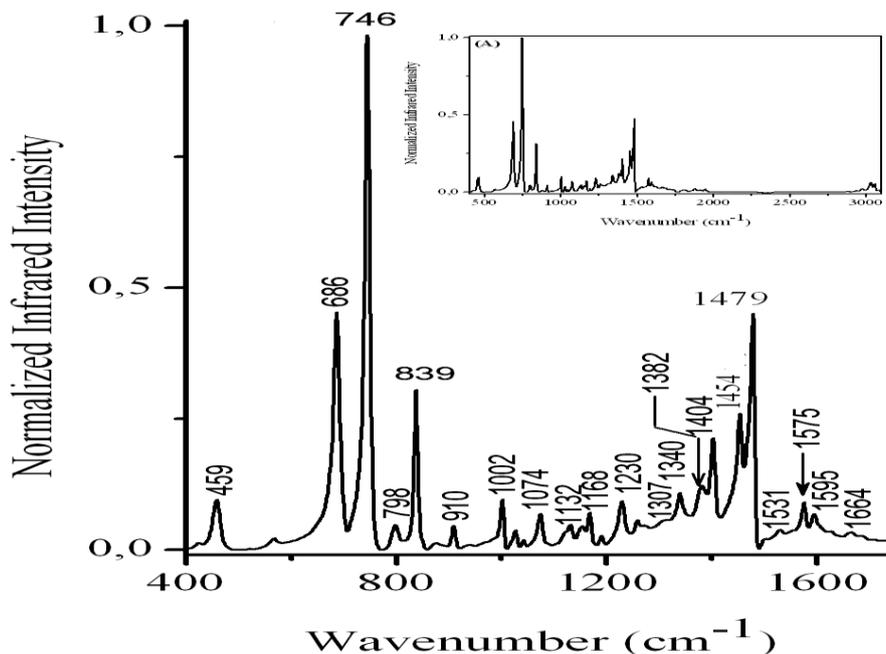


Fig. 3: Experimental normalized infrared spectra of PEcbz-Ter copolymer.

The results are depicted in Table 1. It is well known that the C-H out of plane vibration of para-disubstituted polyphenylenes shifted toward lower frequencies as the chain length increases: it occurs at 837 cm^{-1} for ter-phenyl, 826 cm^{-1} for quarter-phenyl, 818 cm^{-1} for quinque-phenyl and 814 cm^{-1} for sexi-phenyl. In our case, this band appears at 839 cm^{-1} making easy to support the cross-linking between sub-units (Ter and Ecbz). Furthermore, two important peaks located at 1454 and 1479 cm^{-1} . These bands were assigned to the aromatic ring and CH_2 rocking of Cbz moiety, respectively, and probably originated from isolated fractions of Cbz units. The combined results show the presence of bands characteristic of PEcbz centered at (746 cm^{-1} , 839 cm^{-1} , 1002 cm^{-1} , 1032 cm^{-1} , 1074 cm^{-1} , 1230 cm^{-1}), which proves that PEcbz is partially cross-linked. More the spectrum IR of PEcbz-Ter show the essential bands characteristic of PTER located at (459 cm^{-1} , 686 cm^{-1} , 1168 cm^{-1} , 1340 cm^{-1} , 1382 cm^{-1} , 1404 cm^{-1} , 1575 cm^{-1} , 1595 cm^{-1}). Finally, when we compare the infrared results of PEcbz-Ter copolymer, we note the presence of the main characteristic bands of the PEcbz, as well as those of PTER. The whole vibrational analyses supported the copolymerization reaction of PEcbz by polymerized of the Ecbz monomers and its grafting into the Skelton of PTER yielding a new compound alternating Ecbz and Ter motives.

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TABLE 1
INFRARED ASSIGNMENTS OF PECBZ-TER COPOLYMER

<u>PEcbz-Ter</u>		
Freq (cm ⁻¹)	I	Assignments
459	m	Benzene ring deformation
686	s	C-H out of plane bend of terminal mono-substituted benzene rings
746	vs	CH ₂ Rocking- wagging of ethylene group
798	w	C-H out of plane deformation the ring aromatic
839	s	C-H out of plane deformation
910	w	Aromatic out of plane C-H bending
1002/1074	m	Stretching vibration C-C of Ecbz
1132	w	C-H in plane deformation
1168	w	C-H in plane deformation of aromatic ring
1230	m	C-N stretching
1340	w	Torsion of C-H of benzene ring of Terphenyl
1382/1404	vw/m	Stretching vibration of C=C bonds of benzene ring (Ter)
1454	m	Symmetric stretching vibration (C=C) of Ter.
1479	s	C-H deformation in the benzene ring
1575/1595	w	C=C stretching of Benzene ring (Ter)
1664	vw	Quinonoïdal C=C vibration in Ecbz

vs: very strong; s: strong; m: mean; w: weak and vw: very weak

In order to achieve the relationship between structural properties for this copolymer, we studied their optical characteristics (UV-vis absorption and PL emission).

B. Optical absorption and photoluminescence measurements

The absorption spectrum of the new copolymer recorded at ambient temperature in solid state is presented in Fig. 4. The synthesized copolymer absorbs both in the visible and UV-Violet region. In the UV region, part of the electromagnetic spectrum with absorption bands centred at 227 and 312 nm and in the visible part with an absorption band centred at around 500, 616, 682 and 815 nm. The one located at 312 nm is arising from delocalized π - π^* transition in the polymer and the other occurring at 500 nm should originate from a charge transfer state [26]. The effect of the oxidation of the synthesized copolymer is seen in the optical absorption spectrum of PEcbz-Ter, characterized by polaronic/bipolaronic bands located at 815 (1.36 eV). These spectral features are characteristic for organic conducting polymers [27-31]. A wide absorption bands at 815 is observed resulting from the coexistence of polaronic and

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bipolaronic charge carriers, proving the formation of new backbone resulting from the grafting of Poly terphenyl (PTer) into the skeleton of the cross linked PEcbz. As mentioned in [32], PVK absorbs entirely in the UV region ($\lambda_{max} < 350$ nm). So the UV–Vis absorption spectra showed maximum absorption wavelengths of about 312nm. This can be interpreted as π - π^* transition, due to the presence of PEcbz in the copolymer PEcbz-Ter. The extension of the optical absorption in the case of a copolymer (from 400 nm to 800 nm) shows an increase in the conjugation length. The deduction of the optical gap is judged $E_g = 1.48$ eV, which can be identified by extrapolating the linear portion of the wavelength band of the highest (maximum absorption). Moreover, the energy corresponding to the π - π^* transition depends on the delocalization of the π -electrons system. This delocalization is determined by the effective conjugation length, which depends on the amount of structural and conformational defects in the polymer backbone and the interaction between polymer backbones.

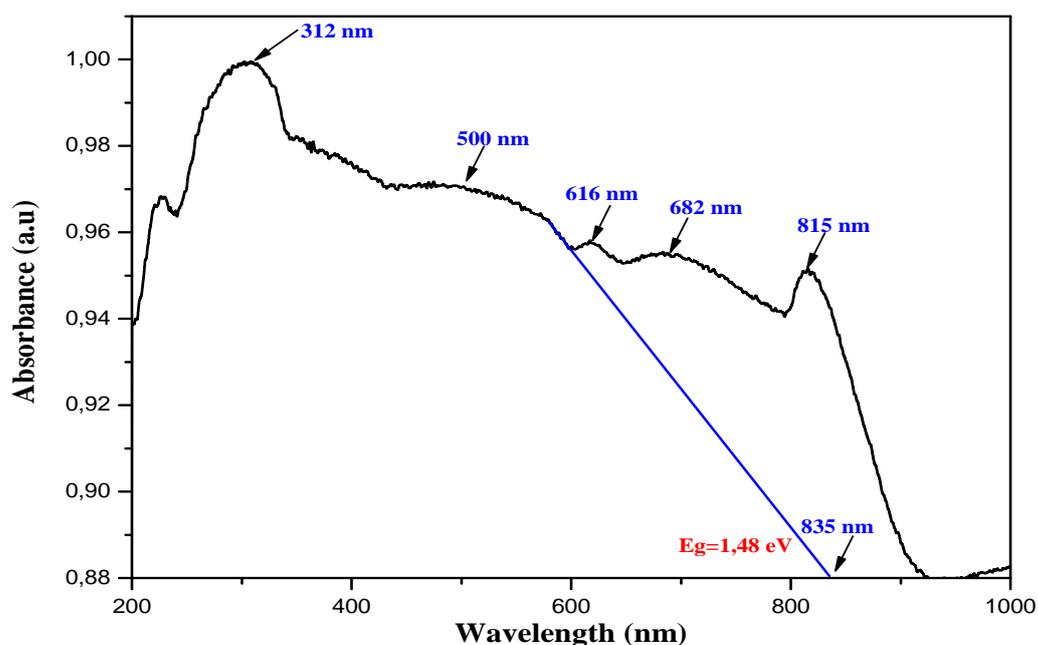


Fig. 4: Normalized UV–Visible optical absorption spectra of PEcbz-Ter powder.

In order to study the photoluminescence properties our copolymer. The powder was collected between two silica plates and excited at 360 nm. PL spectrum of Ecbz-Ter is presented in fig. 5 and characterized by a broad emission situated in the spectral range from 400 to 700 nm, which is constituted of four peaks. This broadening is attributed to the emission from the intramolecular Ecbz excimers. The maximum of the copolymer emission is the more pronounced peaks which appears at 650 nm and is formerly assigned to lower-energy excimers [33]. Lower intensity peaks are located at 457, 575, 607 nm, and slightly depend on the polymer composition. So, we can understand that the most interesting feature in these systems is the strong dependence of the excimer emission intensity on the nature of the copolymer composition. So, we can understand that the most interesting feature in these systems is the strong dependence of the excimer emission intensity on the nature of the copolymer composition. The peaks located between 400 and 500 nm are attributed to the polycarbazole emission [34–38]. On the other hand the redshift compared to the polycarbazole implies an increase of the conjugation length. This increase results from the grafting of terphenyl units. Kinetically, this means that the exciton migration begins in the PVK backbone and continues in the terphenyl moiety.

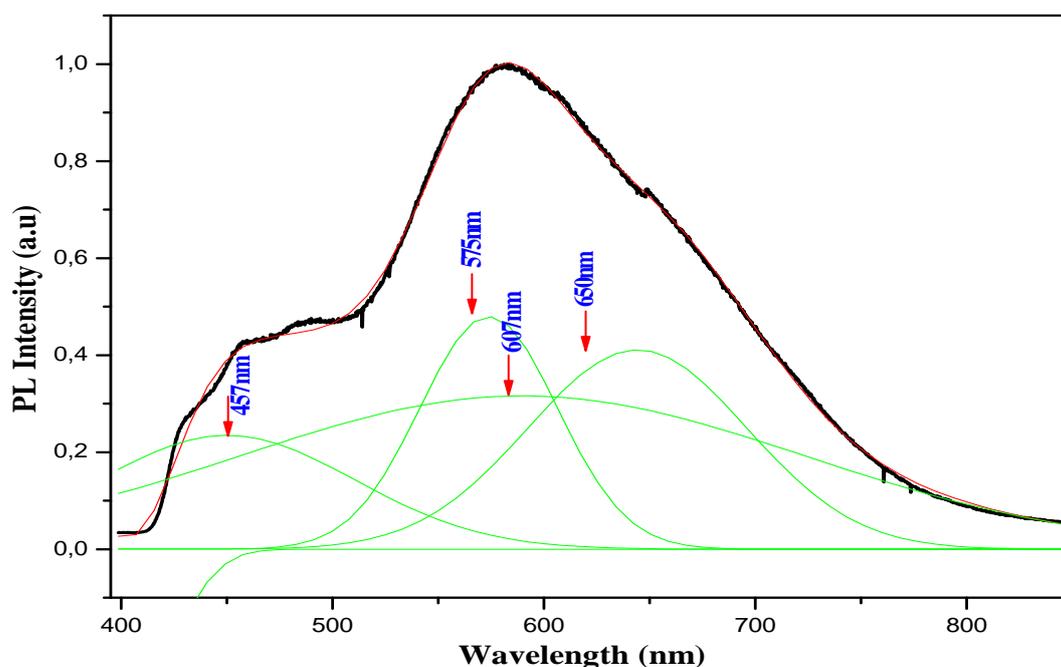


Fig. 5 : Spectres normalises de photoluminescence du PECbz-Ter (Excitation 360 nm).

C. ¹³C NMR spectroscopy and X-ray diffraction (XRD)

The ¹³C NMR spectrum of the studied PECbz-Ter (Fig. 6) confirms the presence of both PECbz and PTer in the obtained structure since it displays two resonance regions. The first one (0–60 ppm) corresponds to the chemical shift of carbons of the aliphatic chain (ethyl and methyl groups), while the second region located between 100 and 150 ppm corresponds to aromatic carbons of carbazole and benzene rings of Terphenyl. In the aliphatic region, the ¹³C NMR spectrum displays three resonance band centred at around 13 and 37-46ppm corresponding, respectively, to methyl group (–CH₃) [39] and methylene (CH₂–) carbons of the ethyl groups of PECbz [40].

In the aromatic region (100-150ppm), the resonance bands centred at about 109, 119.5, 125 and 137.5ppm are assigned to aromatic carbons of the carbazole rings of PECbz. In fact, by comparison with CP-MAS ¹³C NMR spectrum of PVK and that reported in the literature [41], the line centred at 109ppm correspond to carbons C1 and C8 of carbazole rings, then that at 119.5ppm to carbons C3, C4, C4a, C5 and C6 of carbazole rings, the line at 125ppm to carbon C2, C7 and C5a of carbazole rings and the line at 137.5ppm to C1a and C8a. In addition, we note a new resonance band at 129ppm is attributed to aromatic carbon C = C on terphenyl ring. This new resonance band correspond to the presence of fragments the PTer in the copolymer backbone. This confirms well the grafting the reasons for PTer on the chain of PECbz.

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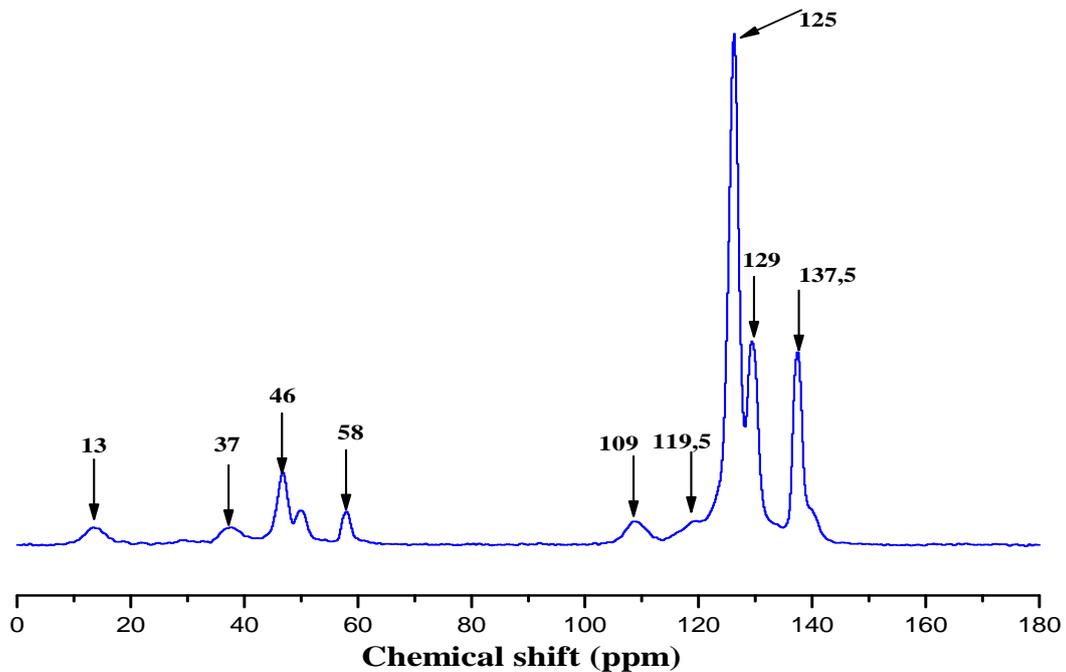


Fig. 6: NMR ¹³C spectra of PEcbz-Ter.

On the other hand XRD patterns of the obtained copolymer PEcbz-Ter prepared by FeCl₃ coupling reaction is shown in Fig. 7.

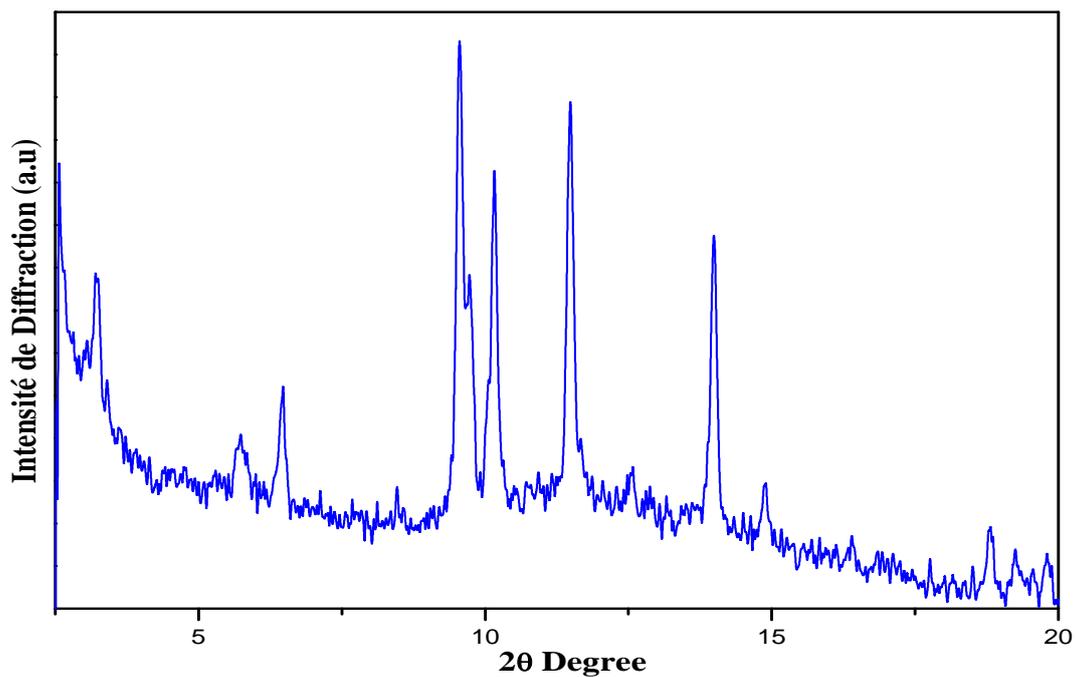


Fig. 7: XRD pattern spectra of PEcbz-Ter copolymer.

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Five major peaks are observed at around 2θ equal to 6° , 9.5° , 10° , 11.5° and 14.5° , these peaks are intensified a marked way. The reflection of low intensity are observed in the region of high angle ($15-20^\circ$), which reflects a new morphology of the copolymer. So, taking account of the Bragg relation, the distance between two successive plans are measured subsequent to 6.47 Å. The most intense peak at 9.5° reflects a structural order in our copolymer (crystalline regions). This can be checked by a study of electronic scanning microscopes and other transmission.

D. Time-resolved photoluminescence TRPL

Reported studies [42-45] generally show a photoluminescence decline longer and longer when the energy emission decreases. Spectrally, this trend is accompanied by a shift in the red issue. These observed changes in the diets of femtosecond or PS are the result of ultrafast migration of excitations that occurred to websites lowest energy during relaxation. This time period often corresponds to a regime where excitations are not yet thermalized. This migration of high energy excitation sites to low energy ones is a consequence of the conjugation length distribution in conjugated polymers. As described above, the images 3D changes in fluorescence over time are supplied from the scanning camera (Camera Steak). The obtained images are shown in Fig. 8, where the wavelength is on the abscissa axis, the decay time on the ordinate one and the intensity is in false colors. PL kinetics of Ecbz-ter, spectrally integrated between 300 nm and 700 nm Based on the 3D images, we represent the evolution of the fluorescence of Ecbz-Ter in the range 0-1ns, the spectra of the dynamic decay is deduced and presented in Fig. 9. It is reported that a mono-exponential model does not reproduce obtained decays; this suggests the presence of multiple excitonic decays. These decays can be reproduced with two non-coupled exponential decays as previously reported [46]. On one hand, referred to previously works [47] for the carbazole $\tau_{mean} = 5.23$ ns, with $\tau_1 = 0.983$ ns and $\tau_2 = 6.223$ ns. The carbazole units are characterized by their longer exciton life-time due to the excimers emission [48]. On the other hand, the decay times are shorter when going from carbazole to the copolymer. For the copolymer, the decay time is close to the temporal resolution, and $\tau_{mean} = 0.436$ ns obtained with $\tau_1 = 0.046$ ns and $\tau_2 = 0.4484$ ns are few significant. It's clearly seen that the charge transfer is more accentuated in the case of copolymer. The carbazole is one of the most interesting functional polymers due to the high transport of the holes, while the terphenyl are characterized by the electron donating units. So we are in the case of a donor-acceptor system which the charge transfer capability is favored in the case of copolymer. The decay of luminescence is mainly due to charge transfer and interchain interaction between polymeric chains established by the insertion of terphenyl which are responsible for exciton migration. This depends significantly on the rate of traps favored by the presence of both units. They are promoting the good non-radiative channel [49].

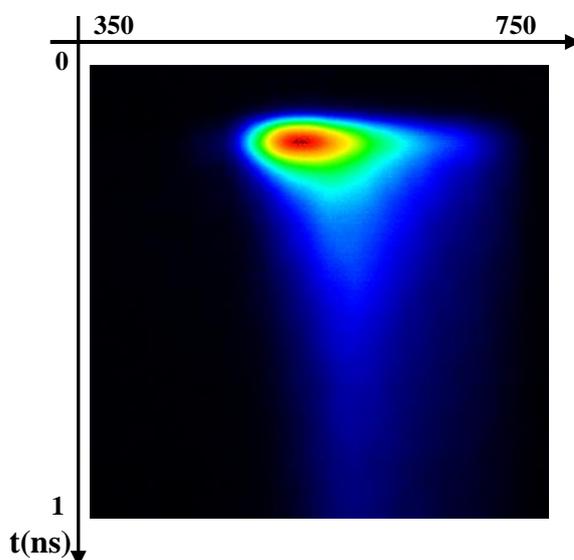


Fig. 8: The 3D-maps TR-PL in false colors of the PEcbz-Ter copolymer.

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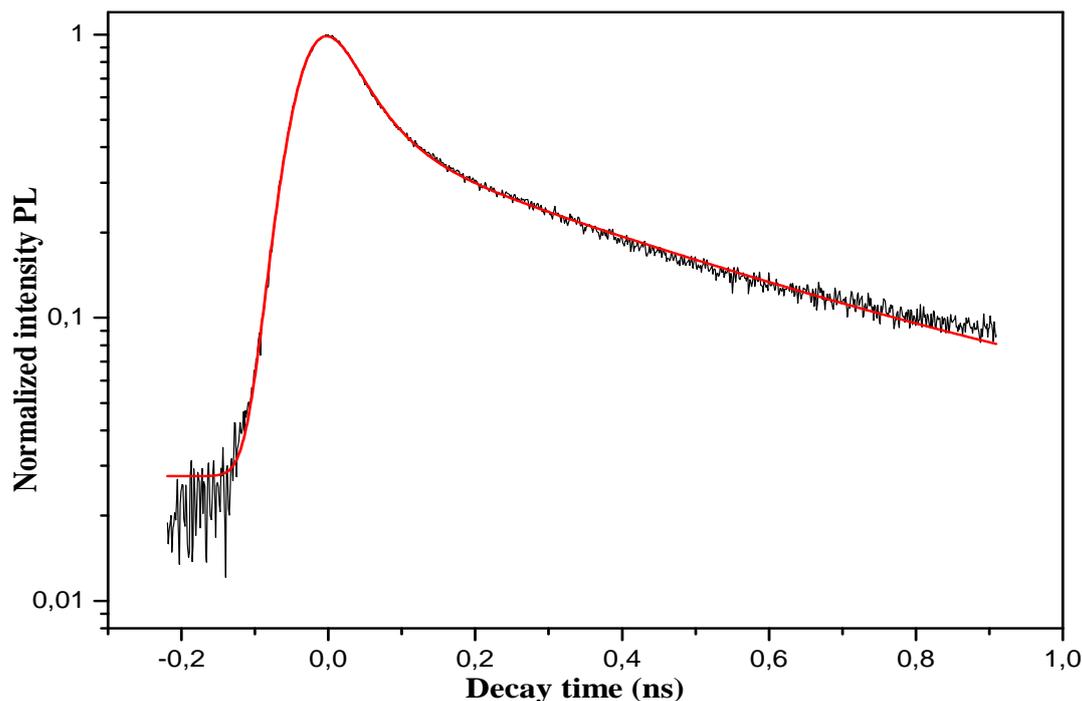


Fig. 9: Time resolved photoluminescence spectra of PEcbz-Ter. The solid lines are fits to the curves.

V. CONCLUSION

We have developed in this work a single procedure to prepare a new organic conjugated copolymer by oxidative copolymerization from two conjugated compounds N-Ethylcarbazole and Terphenyl. The structural parameters, the characterization measurements based on solid state Nuclear Magnetic Resonance (^{13}C NMR), the IR absorption, the UV-visible absorption, the photoluminescence spectroscopy, and X-ray diffraction have been determined. The IR and UV Visible analysis indicate that we have synthesized a new copolymer (PEcbz-Ter) using Ethylcarbazole and terphenyl as starting materials. On the other hand, in order to complete a broader comparative view of optical properties of these two systems and particularly, to investigate the nature of the excited states, their lifetime and decay processes we have report also additional transient photoluminescence (PL) and we have determined the Quantum Yield (QY) of the PL emission for the copolymer. The decay behaviors provide an understanding on how the conformational changes and the chemical nature of the substituent groups can tune the emission properties in such structures and change their QY. Structural and opto-electronic information obtained during this study and the specific properties suggest this new compound to be a good candidate for optoelectronic applications. Finally, due to the interesting physical and chemical properties of this resulting copolymer many experimental and theoretical effort are now undertaken in our laboratory to study other physico-chemical properties of this new copolymer in order to carry out new electronics components (OLED/PLED) based above.

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