



Synthesis and characterization of novel copolymers based on carbazole and anthracene, for optoelectronic applications.

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ABSTRACT

The goal of this work is to study a new copolymer which combines the Ecbz properties and those Ant. First, we describe the route for preparing the new copolymer. Then, we report characterization measurements based on solid-state Nuclear Magnetic Resonance (CP-MAS ¹³C NMR), Raman, IR absorption, UV-visible absorption, photoluminescence spectroscopy, Scanning Electron Microscopy (SEM), and X-ray diffraction.

Indexing terms/Keywords

PEcbz-Ant; RMN; UV-visible absorption; IR; PL; Raman; SEM; and X-ray diffraction.

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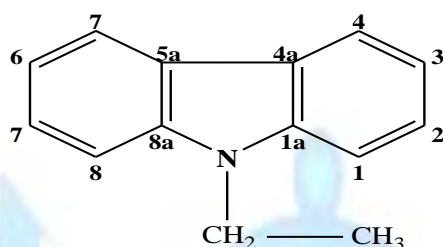
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INTRODUCTION

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], portable electronic [7], lasers [8,9]. 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, in particular, desired in optoelectronic applications such as LEDs or solar cells [10].

In recent years, several studies reported on the synthesis of some blend materials based on poly (N-vinylcarbazole) PVK [11-13], for their interesting physical properties.

In fact PVK absorbs entirely in the UV region and as a consequence of its photoconductivity, its wide band gap [14].

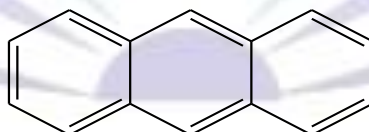


Scheme 1. The chemical structure of Poly(9-ethylcarbazole) (PEcbz)

One of the most important conjugated polymers which allow a very flexible structure and promising properties are poly (Ethylcarbazole-Anthracene). Copolymers containing both poly (9-ethylcarbazole) (scheme1) and anthracene (scheme2) units have also proved to be of interest in combining the properties associated with the two different conjugated rings. This conjugated polymers containing carbazole moieties either in the main or side chains 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 [15, 16]

The necessity of finding new organic materials has caused great concern in scientific community, in this regard. In order to 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 [17-22].

The goal of this work is to study a new copolymer which combines the Ecbz properties and those Ant. First, we describe the route for preparing the new copolymer. Then, we report characterization measurements based on solid-state Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR), Raman, IR absorption, UV-visible absorption, photoluminescence spectroscopy, MEB, and X-ray diffraction.



Scheme 2. The chemical structure of anthracene (Ant)

1. METHODS

Experimental methods

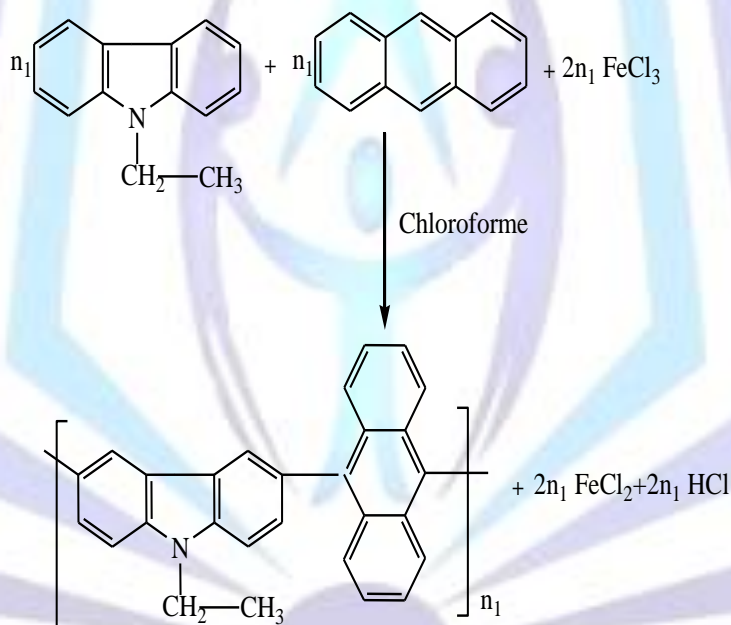
Poly (9-Ethylcarbazole) (PEcbz) powder (97%), Anthracene (Ant) (99%), ferrichloride (FeCl_3), chloroform CHCl_3 (99%), methanol CH_3OH (99,9%), used for the synthesis of the studied compounds were purchased from Aldrich chemistry, A Fisher Scientific International and Riedel-deHaën and were purified before use by usual procedures.

In this work, the copolymer (PEcbz-Ant) 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 an Philips diffractometer available in the laboratory equipped with a curved detector. 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 Bruker 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). $\{^1\text{H}\}-^{13}\text{C}$ CP-MAS (Cross-Polarization Magic-Angle-Spinning). NMR spectra were acquired using a ramp-amplitude sequence [23], a 2 ms contact time, a repetition time of 2 s and a 15 kHz MAS spinning rate. ^1H decoupling during acquisition was achieved using the TPPM method [24] with a radiofrequency (RF) field of approximately 60 kHz. EPR spectra Optical density measurements were carried out at room temperature (RT) using a Cary 2300 spectrophotometer, in the range 200–2200 nm. Continuous-wave (cw) photoluminescence (PL) measurements were collected on a Jobin-Yvon Fluorolog 3 spectrometer using a Xenon lamp (500W) at room temperature. The scanning electron microscope used is environmental-type (ESEM) (FEI Quanta 200 Brand). It is available at National Center for Scientific and Technical Research (CNRS) in Rabat, Morocco. The Raman scattering spectrum was recorded by using an excitation laser wavelength of 1064 nm on a Fourier-Transform Raman spectrometer Bruker RFS 100, with a spectral resolution of 4 cm^{-1} . Infrared absorption measurement was recorded by using a Bruker Vector 22 spectrophotometer. The sample was prepared in pellet of KBr mixed with the organic compound under study and the band positions are expressed in wave-number (cm^{-1}) from 400 to 3500.

2. SYNTHESIS PROCEDURE OF THE COPOLYMER PECBZ-ANT:

The polymerization was developed by a single procedure to prepare a mixture of PEcbz with anthracene (scheme 3). The procedure adopted was to cross link PEcbz by reacting a CHCl_3 solution of PEcbz with anhydrous FeCl_3 and to add a known amount of anthracene (Ant) with undergo polymerization, and the resulting Ant would subsequently participate in copolymer formation process. First, 1.98 g of poly(9-Ethylcarbazole) (PEcbz) was dissolved in approximately 100 ml of CHCl_3 , and then 2 g of anthracene monomers and 5.31 g of FeCl_3 dispersed in 50 ml of chloroform were successively added to the dispersion under stirring. The colour of the solution changed from colourless to green dark then to black dark. 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 kept firstly under pressure for 30 min then under vacuum at 80 $^\circ\text{C}$ for 48 h. A dark black powder was obtained in the fully oxidative (doped) state.



Scheme 3. Synthesis of the PECBz-Ant.

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.

3. RESULTS AND DISCUSSION.

A. Infrared results

Fig.1. Displays experimental normalized optical infrared spectrum of PEcbz-Ant powder in the range of 400–1750 cm^{-1} . First of all, we note that qualitatively the fine structure is a signature of high organized copolymer structure.

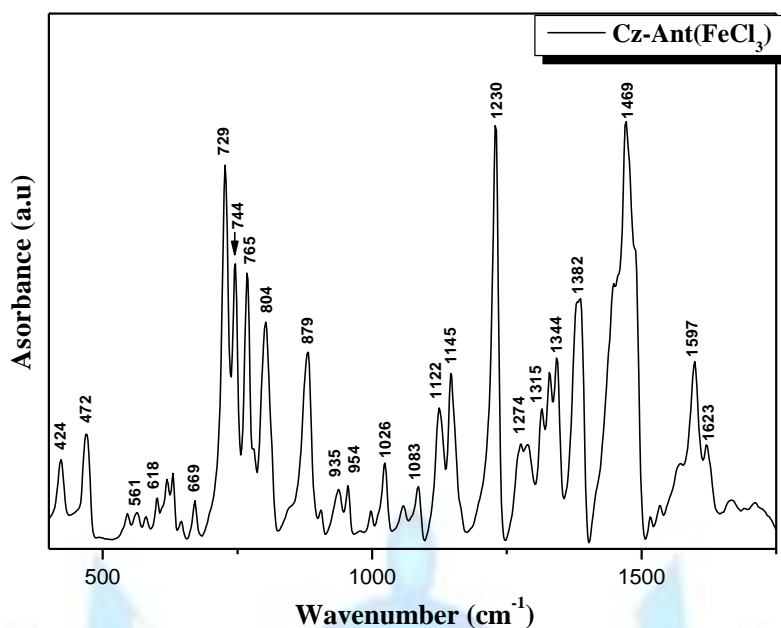


Figure 1: Experimental normalized infrared spectra of PEcbz-Ant copolymer.

The results are depicted in Table 1. Two important peaks located at 1382 and 1469 cm^{-1} . These bands were assigned to the aromatic ring and CH_2 rocking of Cbz.

The combined results show the presence of bands characteristic of PEcbz centered at (744 cm^{-1} , 1026 cm^{-1} , 1083 cm^{-1} , 1145 cm^{-1} , 1230 cm^{-1} , 1597 cm^{-1}), which proves that PEcbz is partially cross-linked. More the spectrum IR of PEcbz-Ant show the essential bands characteristic of Ant located at (472 cm^{-1} , 729 cm^{-1} , 879 cm^{-1}).

Finally, when we compare the infrared results of PEcbz-Ant copolymer, we note the presence of the main characteristic bands of the PEcbz, as well as those of Ant. The whole vibrational analyses supported the copolymerization reaction of PEcbz by polymerized of the Ecbz monomers and its grafting into the Skelton of Ant yielding a new compound alternating Ecbz and Ant motives.

Table 1: Infrared Assignments of PEcbz-Ant copolymer.

PEcbz-Ant		
Freq (cm^{-1})	I	Assignments
472	m	Benzene ring deformation (Ant)
669	m	C-H out of plane bend of terminal mono-substituted benzene rings
729	TF	Ring deformation of substituted aromatic structure (Ant)
744	F	CH_2 Rocking- wagging of ethylene group
765	F	C-H out of plane deformation the ring aromatic
804	F	C-H out of plane deformation the ring aromatic
879	f	Aromatic out of plane C-H bending (Ant)
1026/1083	m	Stretching vibration C-C of Ecbz
1122	m	C-H in plane deformation
1145	m	C-H in plane de formation of aromatic ring
1230	TF	C-N stretching
1315	f	C-H in plane de formation of alkyl group
1344	m	Torsion of C-H of benzene ring
1382	F	Stretching vibration of C=C bonds of benzene ring

1469	TF	C-H deformation in the benzene ring
1597	F	C=C stretching of Benzene ring
1623	f	C-C + C=C stretching

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 Figure 2. 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 261, 302, 352, and 384 nm, and in the visible part with an absorption band centred at around 410, 603 and 891 nm. The one located at 261 nm is arising from delocalized π - π^* transition in the polymer and the other occurring at 410 nm should originate from a charge transfer state in the D-A segment [25]. The effect of the oxidation of the synthesized copolymer is seen in the optical absorption spectrum of PEcbz-Ant, characterized by polaronic/bipolaronic bands located at 891 (1.39 eV). These spectral features are characteristic for organic conducting polymers [26-30]. A wide absorption bands at 891 nm is observed resulting from the coexistence of polaronic and bipolaronic charge carriers, proving the formation of new backbone resulting from the grafting of Poly (Anthracene) into the skeleton of the crosslinked PEcbz. As mentioned in [31], PEcbz absorbs entirely in the UV region ($\lambda_{max} < 350$ nm). So the UV-Vis absorption spectra showed maximum absorption wavelengths of about 261 nm and 302 nm. This can be interpreted as π - π^* transition, due to the presence of PEcbz in the copolymer PEcbz-Ant. 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 $E_g = 3.54$ 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.

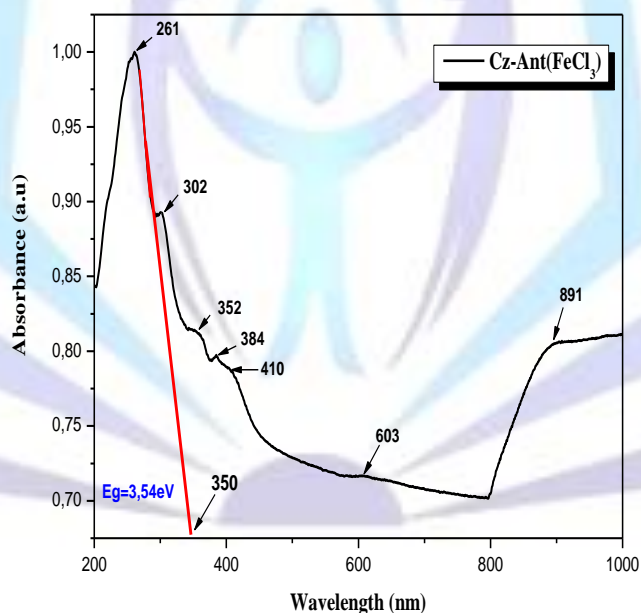


Figure 2: Normalized UV-Visible optical absorption spectra of PEcbz-Ant powder.

In order to study the emission photoluminescence properties of the neutralized copolymer in powder. The powder was collected between two silica plates and excited at 360 nm. PL spectrum of Ecbz-Ant is presented in figure 3 and characterized by a broad emission situated in the spectral range from 400 to 600 nm, which is constituted of two 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 564 nm and is formerly assigned to lower-energy excimers. Lower intensity peaks are located at 489 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.

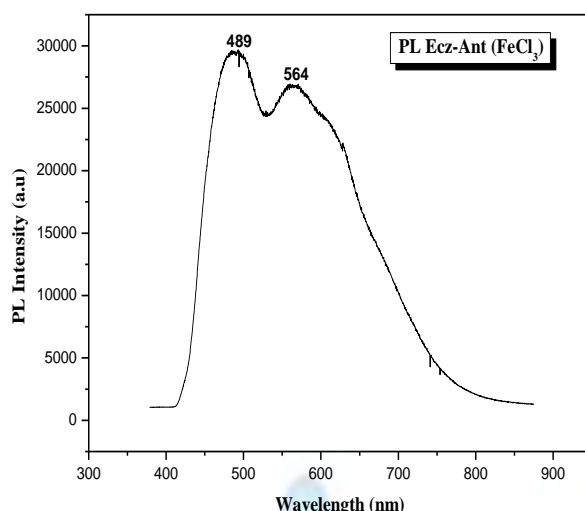


Figure 3: Photoluminescence spectra of Ant-PECbz (Excitation 360 nm).

C. CP-MAS ^{13}C NMR spectroscopy and X-ray diffraction (XRD)

The ^{13}C NMR spectrum of PECbz-Ant (Figure 4), confirms the presence of both PECbz and Ant 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 Anthracene. In the aliphatic region, the ^{13}C NMR spectrum displays three resonance band centred at around 13 and 37–46 ppm corresponding, respectively, to methyl group ($-\text{CH}_3$) [32] and methylene (CH_2-) carbons of the ethyl groups of PECbz [33].

In the aromatic region (100–150 ppm), the resonance bands centred at about 108, 125 and 139 ppm are assigned to aromatic carbons of the carbazole rings of PECbz. In fact, by comparison with CP-MAS ^{13}C NMR spectrum of PVK and that reported in the literature [34], the line centred at 108 ppm correspond to carbons C1 and C8 of carbazole rings, the line at 125 ppm to carbon C2, C7 and C5a of carbazole rings and the line at 139 ppm to C1a and C8a.

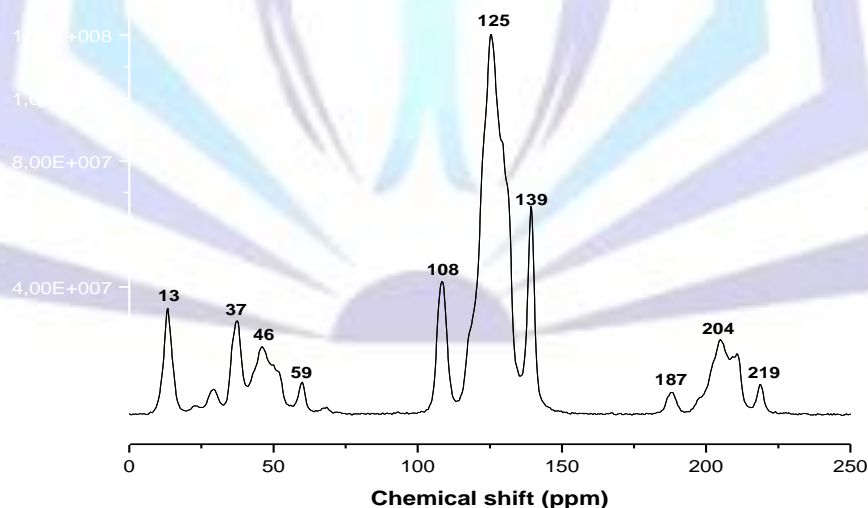


Figure 4. NMR ^{13}C CP-Mass spectra of PECbz-Ant.

The XRD patterns of PEcbz-Ant prepared by FeCl_3 coupling reaction are shown in Fig.5.

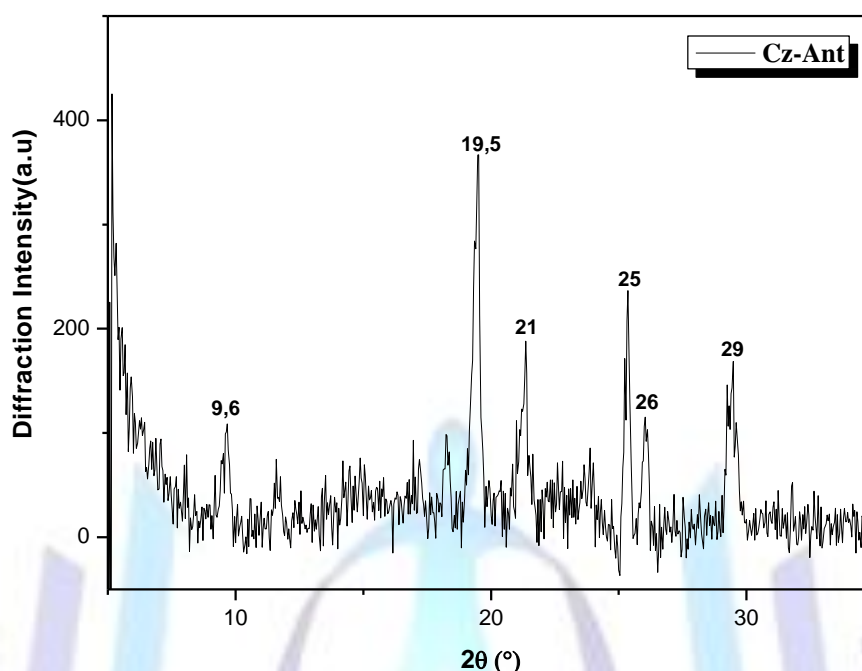


Figure 5: XRD pattern spectra of PEcbz-Ant copolymer.

Six major peaks are observed at around 2θ equal to 9.6° , 19.5° , 21° , 25° , 26° and 29° these peaks are intensified a marked way. The reflection of low intensity are observed in the region of high angle ($2\theta = 30-35^\circ$), which reflects a new morphology of the copolymer. The most intense peak at 19.5° reflects a structural order in our copolymer (crystalline regions). This can be checked by a study of electronic scanning microscopes and other transmission.

D. PLRT

Reported studies 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 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 figure 6, where the wavelength is on the abscissa axis, the decay time on the ordinate one and the intensity is in false colors. The spectrum PL is calculated by integrating the signal over the entire image.

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 [35,36]. The decay of luminescence is mainly due to the conjugation length established by training bicarbazole units and insertion of anthracene ones which are responsible for exciton migration in the polymeric chain. This depends significantly on the rate of traps favored by the presence of both units. They are promoting the good non-radiative channel [37].

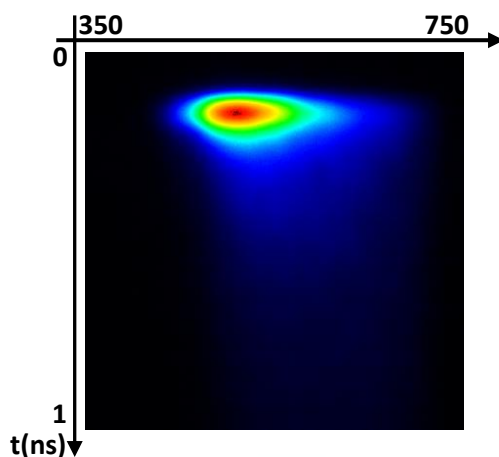


Figure 6: 3D images obtained for the PLRT copolymer ECBZ Ant (FeCl_3)

Table 2: Time-resolved PL of copolymer EtCbz-Ant (FeCl_3)

	T1 (ns)	T2 (ns)	T(average) (ns)
EcZ-Ant (FeCl_3)	0.039	0.320	0.319

From the given results it is clear that the synthesis with FeCl_3 produces less defects causing a decline in luminescence in a very large time ($T(\text{average}) = 0.319 \text{ ns}$).

E. Scanning Electron Microscopy (SEM):

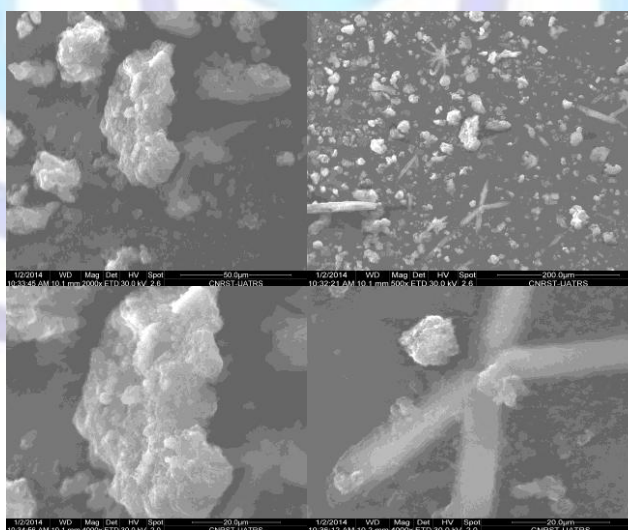


Figure 7: SEM of EtCbz-Ant (FeCl_3)

In Figure 7, we present a SEM of the EtCbz-Ant (FeCl_3) in which we can clearly see the presence of mainly crystalline domains, together with small amorphous regions. This agrees with X-ray data which suggest rather short coherence lengths. However, we also note the presence of aggregates of heterogeneous size.

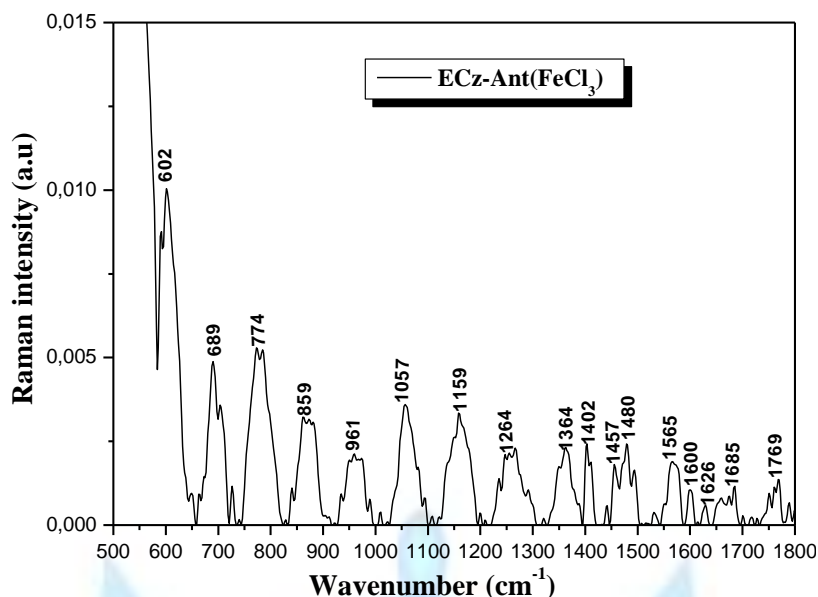


Figure 8: Raman spectrum of EtCbz-Ant (FeCl₃)

In Figure 8, we present Raman spectra of EtCbz-Ant (FeCl₃). It can be seen the results depicted in Table 3.

Table 3: Raman Assignments of PEcbz-Ant copolymer.

Freq (cm ⁻¹)	Assignments
602	In-plane ring deformation
774	Ring vibration
859	CH deformation
961	Ring "breathing"
1057	C-H in-plane deformation
1264	C-N stretch
1457	CH ₃ , CH ₂ deformations
1480	Ring stretch
1565	C=C stretch
1600	Ring stretch

We note the presence of vibrational transitions corresponding to the anthracene and ethylcarbazole, particularly the groupements CH₃/CH₂ and C-N respectively at 1457 and 1264 cm⁻¹ of ethylcarbazole compound, showing the formation of the copolymer EtCbz-Ant and confirming the results previously obtained by other techniques (IR, XRD, SEM, ...).

5. CONCLUSION

In this paper, we describe the synthesis of a new organic graft copolymer based on EtCbz and Ant. The characterization based on solid-state Nuclear Magnetic Resonance (CP-MAS ¹³C NMR), Raman spectroscopy, IR absorption, UV-visible absorption, photoluminescence spectroscopy, SEM, and X-ray diffraction.

We can group these results of characterisations as follows:

*The Infrared and Raman results of PEcbz-Ant copolymer, show the presence of the main characteristic bands of the PEcbz, as well as those of Ant.

The UV-Vis absorption spectra showed maximum absorption wavelengths of about 261 nm and 302 nm. This can be interpreted as π-π transition, due to the presence of PEcbz in the copolymer PEcbz-Ant.



*The study of the emission photoluminescence properties reveal 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 ^{13}C NMR spectrum of PEcbz-Ant, confirms the presence of both PEcbz and Ant in the obtained structure since it displays two resonance regions.

* The most intense peak at $2\theta=19.5^\circ$ in XRD spectra reflects a structural order in our copolymer (crystalline regions). This can be checked by a study of electronic scanning microscopes in which we can clearly see the presence of mainly crystalline domains, together with small amorphous regions.

So, the formation of Ant and its grafting into the skeleton of EtCbz to form a new homogenous and compact material is confirmed. These polymeric hybrids exhibit modified properties as compared to the departure components their pristine components.

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