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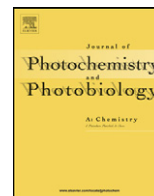


Photo- and electroluminescence in a series of PPV type terpolymers containing fluorene, thiophene and phenylene units

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ABSTRACT

The emissive properties of terpolymers with fluorene, thiophene and phenylene groups, forming alternating PPV type structures, are discussed in terms of their composition, photo- and electroluminescence properties. The fluorene groups were inserted in each phenylene–vinylene and thiophene–vinylene units, and their concentration did not vary, representing 50% of the molar composition. The ratio of thiophene–vinylene/phenylene–vinylene varied in the range 25, 50 and 75%. Photo- and electroluminescence properties were strongly dependent on the thiophene–vinylene content and were compared with the fluorene–vinylene–thiophene and fluorene–vinylene–phenylene parent copolymers.

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1. Introduction

The correlations between light emission processes with chemical structure and morphology is of prime importance for the comprehension of the operating phenomena in the various optoelectronic devices and related applications of electronic polymers [1,2]. The chemical linking of monomers in copolymerization or the mixing of polymers in blend fabrication [3] are powerful tools to tune light emission and output yield in LEDs [4,5] and photovoltaic efficiency in solar cells [6,7] apart from other applications.

In order to get a copolymer with good properties for electronic devices, several properties must be controlled or must be taken into consideration. Some of them are intrinsic to the chemical structure, defining the band gap, whereas others are related to the processing (materials should be soluble to be processed from solutions), some are related to the morphology, involving interchain and intrachain interactions. Depending on the type of the device, these complex set of properties must be differently optimized. In the present contribution two widely explored monomers were used: fluorene and thiophene, in combination with phenylene, in an alternating PPV type structure, namely

poly[(9,9-dihexyl-9H-fluorene-2,7-diyl)-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl]_x-alt-[(9,9'-dihexyl-9H-fluorene-2,7-diyl)-1,2-ethenediyl-2,5-thiophene-1,2-ethenediyl]_y (LaPPS30). This is an example of copolymer that combines a wide electronic absorption spectrum, a good solubility in several organic solvents, and the possibility of several types of energy transfer from the fluorene–vinylene to the thiophene–vinylene units, and thus it is potentially useful for several optoelectronic devices. For example, in a recent contribution the photovoltaic properties of this material containing CdSe nanoparticles were reported [8].

In general, the photoluminescence properties in dilute solutions of a multichromophoric conjugated copolymer will depend on the energy gap of each lumophore and several types of intrachain photophysical processes may arise from the primarily excited center. For example, intrachain energy transfer, energy migration and conformational relaxation processes in conjugated copolymers are complex phenomena which strongly depend on chemical structure and chain conformation. For polymer with donor and acceptor units, charge separation after excitation is a very efficient process and polymers with these groups are potentially useful in photovoltaics [9,10]. Literature data on conjugated terpolymers report mainly on systems based on Suzuki cross coupling or Yamamoto polycondensations that is, without double bonds between the chromophores. Examples are the DA structures poly(9,9-dihexylfluorene, 10-hexylphenothiazine

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9-fluorenone) [11], the copolymers based on 9,9-dioctylfluorene, 4,7-dithienyl-2-yl-2,1,3-benzothiadiazole, and (oligo)thiophene units [12] segmented configurations with blocks of varying length poly {[3,6-(9-(1-ethylpentyl)-9-octylfluorene)]-co-[bis(biphenyl-4-yl)phenylamine)-4',4'-diyl]} [13] for LEC fabrication and the π -conjugated backbone consisting of 75 mol% fluorene and 25 mol% 5,5'-diphenyl-2,2'-bi-1,3,4-oxadiazole with 2-(2-(2-methoxyethoxy)ethoxy)ethyl groups attached on the 9-C of the fluorene moieties [14]. In the majority of cases, a specific application is sought, and they are not focused on a mechanistic interpretation of the photophysical processes. In this contribution we report on terpolymers prepared via Wittig polycondensation, which leads to chains with double bonds linking the repeating units and the main purpose was to explore the nature of the photophysics involved. It is noteworthy that LaPPS30 structure is reported for the first time. Moreover, since the reactivity of the monomers may vary, the terpolymers composition may differ from that of the feed composition used in the polymerization reaction medium. Since this is not a trivial issue we have reported previously the detailed NMR quantitative characterization of the LaPPS30 series [15].

LaPPS30-X (where X stands for content of thiophene–vinylene units) is a set of copolymers which may have its optical and electronic properties modified by changing the relative ratio of its fluorene–vinylene–phenylene and fluorene–vinylene–thiophene units. Because these two units have different optical band gaps, energy transfer by different mechanisms from the donor (fluorene–vinylene) to the acceptor (thiophene–vinylene) units may occur. The efficiency of this process is strongly dependent on several parameters, including the spectral overlap between emission and absorption bands of the involved species [16]. Moreover, since these two units may be forced into planarity by the vinylene groups [17], the probability of energy transfer from the donor to the acceptor will also depend on the size and on the relative orientation of both units that are held together. These processes were studied in polymeric solutions following both steady-state emission processes and dynamics of the emission decays.

When in solid state, in addition to the intrachain energy transfer and charge transfer processes, interchain photophysical processes also play important roles due the possibility of polymer aggregation, a very common process in both polyfluorenes and polythiophenes [18–27]. In photoluminescence (PL), along with the emission of isolated chains, emission of aggregates may be possible in some cases, whereas in others the quenching of the emission is the most important process. In electroluminescent (EL) processes the emission spectrum is in most cases very similar to that of photoluminescence, but may also be different [4]. When they are similar, we might assume that the same type of exciton is formed. Here the EL and PL profiles for the materials with different compositions will be compared and analyzed in terms of the copolymer structure.

2. Experimental

2.1. Polymer synthesis

The LaPPS30 series was prepared following the Wittig route, as described with detail in Ref. [15]. Briefly, the phosphonium bromide derivative of 9,9'-dihexyl fluorene reacted with terephthalaldehyde and 3,5-thiophene dialdehyde in different ratios. For the parent “homopolymers”, that is, copolymers without phenylene (LaPPS30-100) and without thiophene (LaPPS30-0) the same route was followed omitting the addition of one of the aldehydes, as described in Refs. [3,28], respectively.

2.2. Equipment and methods

The molar masses of the copolymers were measured by a gel permeation chromatograph Agilent 1100 equipped with a refractive index detector and PL gel mixed C and B columns in series, at 35 °C, using DMF as solvent and monodisperse polystyrene samples as standards.

A Netzsch TG-204 F1 differential scanning calorimetry was used to measure the thermal properties of materials following ASTM D 3418 method standard. The calorimeter operated with a nitrogen flow 15 cm³ min⁻¹ at heating rate of 10 °C min⁻¹. The temperature range observed was 20–200 °C.

Absorption spectra in the UV–vis range (250–800 nm) were acquired with a double beam Shimadzu spectrophotometer model UV 2401 PC.

Steady-state PL spectroscopy was performed in a UV 2401 PC Shimadzu spectrophotometer, double beam. For solutions a square cuvette of 1 cm was used. Films were supported on glass slides and the emission spectra were recorded using a front-face sample orientation. Slits were selected for a spectral resolution of ± 1 nm in excitation and in emission. The PL quantum yields of the polymers in solution were estimated by using a 10⁻⁵ mol L⁻¹ solution of 9,10-diphenylanthracene as standard [29].

Fluorescence decays were recorded using single photon counting technique with an Edinburgh Analytical nF900 system operating with a pulsed hydrogen lamp (repetition rate 40 kHz), $\lambda_{\text{exc}} = 350$ nm, $\lambda_{\text{em}} = 514$ nm, $\lambda_{\text{em}} = 525$ nm and $\lambda_{\text{em}} = 562$ nm. A 1 cm square cuvette was used for solutions, which were saturated with nitrogen. For films, a rectangular cuvette was employed containing films under vacuum (10⁻³ Torr). Ludox was used to collect the instrumental response. The sample decay and the instrumental response were deconvoluted using software provided by Edinburgh. Data treatment was carried out using exponential functions (Eq. (1)) and the fitting was considered adequate when simultaneously the residual distribution is random and the χ^2 parameter is close to 1:

$$F(t) = \sum_{i=1}^n B_i \exp \left[-\frac{t}{\tau_i} \right] \quad (1)$$

where B_i is the weight factor for every decay τ_i .

2.3. Device preparation

Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) (Bayer Corporation) was deposited by spin-coating onto a glass plate covered with ITO blend (OFC Corporation, 20 Ω sq⁻¹), dried at 100 °C for 1 h under vacuum. A chloroform polymer solution (20 mg mL⁻¹) was filtered and deposited by spin-coating over the PEDOT:PSS layer, under dry nitrogen at 2000 rpm. The polymer films were typically 75 nm thick. A metallic calcium layer (400 nm thickness) was deposited on top of the polymer layer by sublimation at 10⁻⁷ Torr, followed by a protective layer of aluminum on top. The final configuration of the device was ITO/PEDOT:PSS/polymer layer/Ca/Al.

The devices were characterized using a system described previously [30]. The electroluminescence characterization of the devices was done with an Oriel monochromator 78200 and a calibrated photometer International Light Inc., model IL 1400a, under argon.

3. Results and discussion

3.1. Copolymer characterization

Taking into account that in copolymers the final composition is not always the same as the feed composition of the reaction

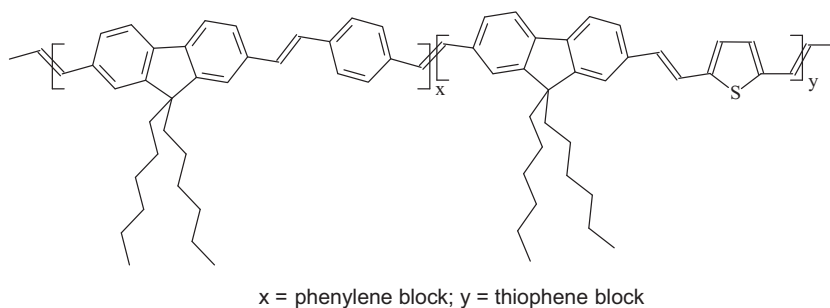


Fig. 1. Chemical structures of the LaPPS30 series: poly[(9,9-dihexyl-9H-fluorene-2,7-diyl)-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl]-alt-[(9,9'-dihexyl-9H-fluorene-2,7-diyl)-1,2-ethenediyl-2,5-thiophene-1,2-ethenediyl] (LaPPS30).

Table 1

The reaction feed composition and the copolymers molar composition.

Polymer	Phenylene/thiophene x/y theoretical ^a	Phenylene/thiophene x/y experimental ^b	T _g (°C)	Mw (g mol ⁻¹)	PD ^c
LaPPS30-0	100/0	100/0	123	10,000	2.03
LaPPS30-25	75/25	63/37	107	22,000	3.40
LaPPS30-50	50/50	52/48	73	10,200	2.01
LaPPS30-75	25/75	40/60	108	17,000	1.95
LaPPS30-100	0/100	0/100	95	7700	1.72

^a Molar composition in reaction feed.

^b Copolymer molar composition.

^c Polydispersivity.

medium, a detailed NMR analysis (using the Cross Polarization Magic Angle Spinning method) of the terpolymers was performed to determine the real materials composition [15] their general structure is depicted in Fig. 1. In Table 1 the composition of the reaction feed and that of the resulting copolymers is shown. The fluorene groups were inserted in each phenylene–vinylene and thiophene–vinylene units, and thus did not vary, representing 50% of the molar composition. Since no significant differences between those values were found, the acronyms for the copolymers follow the theoretical composition, to facilitate the reading.

The molar masses and polydispersities by GPC are also in Table 1. In a general manner, conjugated polymers do not present large molar masses. Strictly speaking, a substantial number of the published works are related to oligomers [31]. The present results are not far from the usual found for useful electronic polymers.

3.2. Photoluminescence properties in solution

The electronic absorption spectra of chloroform solutions (10⁻⁵ molL⁻¹), shown in Fig. 2, are composed by broad bands, except for the LaPPS30-100, a fluorene–thiophene copolymer, which showed a partially resolved vibronic structure. In principle, the absorption at higher energy may be attributed to the fluorene–vinylene units and the absorption at lower energy to the thiophene–vinylene units but the peak position of these two blocks will vary according to the specific composition. The most prominent feature is the occurrence of a red shift, which is brought about by the progressive incorporation of the thiophene units, also observed for other polythiophenes [32]. Vibronic structure that arose in thiophene polymers was associated with their chain planarity of the isolated chains. No red-edge bands due to the excitonic splitting by the presence of aggregates [32,33] were observed attesting the good quality of the solvent chosen for the measurements. Spectral data are compiled in numerical form in Table 2.

The LaPPS30 PL spectra in chloroform solution (Fig. 3) are not a mirror image of the absorption. The profile and peak position of the photoluminescence spectra depend on the relative amount of the thiophene–vinylene components. LaPPS30-0 (a fluorene–vinylene copolymer) shows a partially resolved vibronic emission band

with two peaks: at 474 nm (0-0 band) and 499.8 nm (0-1 band). Copolymers containing 25% and 50% of fluorene–thiophene units (LaPPS30-25 and LaPPS30-50, respectively) showed two emissions, a weaker component coincident with the LaPPS30-0 0-0 band (its intensity decreases with the fluorene–thiophene component in accordance with their absorbances) and a lower energy component, with higher intensity, centered respectively at 505.5 and 512 nm. This second component has not depicted vibronic structure. As occurred for the absorption spectra, PL also shifts to the red as the content of fluorene–thiophene component increases. Moreover, vibronic structure arises for the copolymer with 75% of fluorene–thiophene (LaPPS30-75) and becomes well resolved for LaPPS30-100 (0-0 band at 526.9 nm and 0-1 band at 550 nm). It is noteworthy that for LaPPS30-75 and LaPPS30-100, the PL spectra are mirror images of the absorption, indicating that the conformational relaxation is less relevant for both and that their decays take place from lumophores with similar geometry. This result is

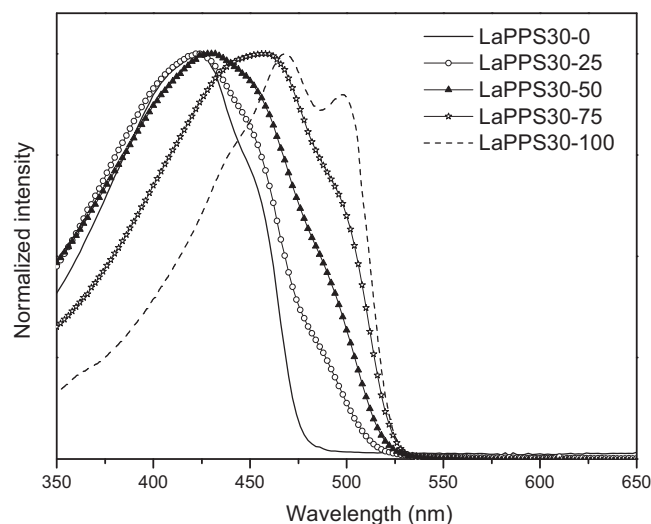


Fig. 2. Electronic absorption spectra of LaPPS30 series in chloroform solution 10⁻⁵ molL⁻¹.

Table 2
Electronic absorption and emission wavelengths for the copolymers in solution (chloroform 10^{-5} mol L $^{-1}$) and films.

λ_{max} (nm)	Abs λ_{max} (nm) 10^{-5} mol L $^{-1}$	Abs λ_{max} (nm) solid state	PL λ_{max} (nm) 10^{-5} mol L $^{-1}$	PL λ_{max} (nm) solid state	ε (L cm $^{-1}$ mol $^{-1}$)	PL quantum yield Φ_f
LaPPS30-0	424	410	477, 499	482, 512	44,859	0.88
LaPPS30-25	430, 453	412	480, 505	512	43,616	0.85
LaPPS30-50	430	423	480, 512	526	31,235	0.24
LaPPS30-75	460	431	516, 548	530	32,027	0.33
LaPPS30-100	468, 497	440	526, 550	533	44,123	0.50

probably associated to the chain planarization induced by the thiophene units in copolymers with higher content of these units.

The emission of polymers and copolymers containing more than one photoactive group very often leads to a unique emission because of the highly efficient energy transfer by energy migration, by resonant non-radiative energy transfer or by electron transfer processes [1,34]. The efficiency of these processes depends on the proximity between the donor and acceptor groups, on the spectral overlap and on a suitable orientation of the involved species [16,35]. The presence of two emission bands in some of these copolymers (LaPPS30-25 and LaPPS30-50) indicates that some of those requirements were not fulfilled. By inspecting the LaPPS30-100 electronic absorption band and the LaPPS30-0 PL band, we may conclude that the emission of the fluorene–vinylene segments are strongly overlapped with the absorption band of the fluorene–thiophene segments, which is one of the requirements for the resonant non-radiative energy transfer process. Thus, it may be concluded that there are structural constraints, which inhibited the complete energy transfer processes from the higher energy absorbing groups to the lower energy component. These constraints may arise from the alternated structure of the copolymer or by the breaking of the conjugation along the main chain.

The fluorescence decays were recorded for all copolymers in chloroform solutions (10^{-4} mol L $^{-1}$) and were analyzed using exponential functions. All of the samples were excited at 350 nm. In the first set of experiments the emission decay was taken at the maximum of the emission band of each copolymer. In the second set of data the decay was collected at lower energy.

The LaPPS30-0 decay at $\lambda_{\text{em}}=475$ nm (emission peak) is bi-exponential with a predominant faster component $\tau_{1\text{PL}}=1.02\pm 0.01$ ns (85%) and a slower component with $\tau_{2\text{PL}}=2.33\pm 0.07$ ns (15%) (Table 3). It has been reported that this longer decay is related with oxidation of the polymer chain

[3,36]. Nevertheless, this hypothesis was not considered in the present case because the 9 positions in the fluorene ring, which is the locus for oxidation is already substituted by alkyl branches. Additionally no signal was seen either in the FTIR or in RMN spectra that could be ascribed to any kind of chemical alteration. This second longer component was thus attributed to interacting chains, since there are several indications that LaPPS30-0 can easily undergo aggregation even in relatively low concentrated solutions [26,27], as noted.

The PL decay of LaPPS30-100 is monoexponential with $\tau_{\text{PL}}=1.18\pm 0.03$ ns when the signal is collected at $\lambda_{\text{em}}=550$ nm (emission peak). Lifetime values of 1–2 ns have been reported for the emission decays of polythiophene isolated chains [21,23,37].

Taking into account this two set of data, for LaPPS30-0 and LaPPS30-100, one should expect for the LaPPS30-X terpolymers that if intrachain energy transfer or electron transfer processes will occur from the fluorene–vinylene blocks toward the thiophene–vinylene ones, the donor emission would be completely quenched or its life time decreased to some extent if some emission still remains. Thus, to analyze the decays for the terpolymers, two informations, that from the steady-state PL and the lifetimes must be combined.

Biexponential decays were observed for LaPPS30-25 when the emission is collected at $\lambda_{\text{em}}=475$ nm (emission peak), with a faster components of 1.33 ± 0.04 ns (88%) and a slower component of 3.6 ± 0.3 ns (12%) (Table 3). As the steady-state PL showed, the emission at 475 nm is predominantly due to the fluorene–vinylene blocks, but the contribution of the blue-edge of the thiophene–vinylene component cannot be, in principle, excluded. The faster component is observed in the same time range of other polyfluorenes as well as of other polythiophenes, but the longer component is higher than that observed for LaPPS30-0 ($\tau_{1\text{PL}}=2.33\pm 0.07$ ns). The contribution of this longer component increases from 12% to 20% when the sample is excited at the red-edge band of the copolymer ($\lambda_{\text{em}}=527$ nm). Although longer decays can in principle be attributed to aggregates [37], time resolved emission experiments using different excitation wavelengths; different concentrations and solvents with different solvation capability should be required for their unequivocal assignment. Studies are in progress.

LaPPS30-50 emission decay collected at $\lambda_{\text{em}}=475$ nm (low intensity blue shoulder of the emission peak) is also biexponential, with a component of 0.86 ± 0.03 ns with a larger contribution (75%), and a slower component of 2.29 ± 0.07 ns (25%) (Table 3). A decrease of both lifetimes was observed for emission at $\lambda_{\text{em}}=527$ nm (second emission peak) in addition to the enhancement of the contribution of the longer component (from 25% to 40%). When monitored at $\lambda_{\text{em}}=550$ nm where the thiophene–vinylene blocks should be emitting predominantly, LaPPS30-50 showed a faster decay with a lifetime very similar to the LaPPS30-100 (1.20 ± 0.03 (88%)) and a longer component similar to the longer component of the LaPPS30-25 (3.2 ± 0.2 ns (12%)). Based on these data and on the steady-state PL, we may consider that when the fluorene–vinylene is preferentially monitored, the decays are faster than that for LaPPS30-0 suggesting the possibility of a partial energy transfer processes from this block to that

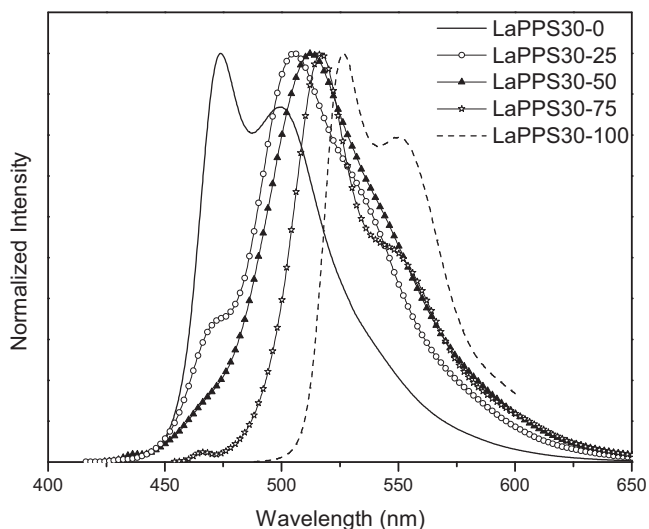


Fig. 3. Photoluminescence spectra of the LaPPS30 series in chloroform solutions 10^{-5} mol L $^{-1}$.

Table 3

Fluorescence decays of the LaPPS30 series in chloroform solutions ($1 \times 10^{-4} \text{ mol L}^{-1}$) using $\lambda_{\text{exc}} = 350 \text{ nm}$; B is the contribution of every lifetime to the entire decay, χ^2 measures the quality of the exponential fitting.

Materials	λ_{em}	τ_1 (ns)	B (%)	τ_2 (ns)	B (%)	χ^2
LaPPS30-0	475	1.02 ± 0.01	85	2.33 ± 0.07	15	1.238
LaPPS30-25	475	1.33 ± 0.04	88	3.6 ± 0.3	12	1.016
	527	1.19 ± 0.04	80	3.0 ± 0.2	20	1.019
LaPPS30-50	475	0.86 ± 0.03	75	2.29 ± 0.07	25	1.043
	527	0.72 ± 0.05	60	1.89 ± 0.05	40	1.098
	550	1.20 ± 0.03	88	3.2 ± 0.2	12	1.102
LaPPS30-75	550	1.18 ± 0.01	100			1.163
LaPPS30-100	550	1.18 ± 0.03	100			0.933

of thiophene–vinylene. When the thiophene–vinylene groups are preferentially monitored, the decay is similar to that for LaPPS30-100.

LaPPS-30-75 and LaPPS30-100 decay monoexponentially, with very similar lifetimes: $\tau_{\text{PL}} = 1.02 \pm 0.01 \text{ ns}$ and $\tau_{\text{PL}} = 1.18 \pm 0.03 \text{ ns}$, respectively. When the decay profiles with the PL emission for the LaPPS30-25, LaPPS30-50 and LaPPS30-75 are compared, it was noted that for LaPPS30-25 and LaPPS30-50 there is a double emission in the PL spectra and a bi-exponential decay and for the LaPPS30-75 there is only one emission band and a mono-exponential decay. Because of the biexponential decays of LaPPS30-25, LaPPS30-50 and LaPPS30-0 and the monoexponential decay of LaPPS30-75, and LaPPS30-100, we may consider that these two set of polymers have different distribution of the segments or different chain conformations that influence differently the intrachain energy transfer process. It seems that in LaPPS30-25 and LaPPS30-50 the fluorene–vinylene segments are only partially transferring their energy to the fluorene–thiophene segments.

3.3. Photoluminescence in solid state

Electronic absorption spectra of all films are shown in Fig. 4. Again there is a red-shift of the main peak with increases in the content of fluorene–thiophene units. Compared to the absorption in solution all of the spectra are broader. This suggests that in films there is a higher conformational disorder generating chains with a broader distribution of conjugation lengths, each of them absorbing in different energy. Compared to solutions, a small spectral blue-shift for all terpolymers has also been observed. In general, the spectral shift from the solution to film is strongly dependent

on two different contributions: one is the possibility of aggregation, and blue-shift in absorption should be expected if J-aggregates are formed; the other is related to changes in chain conformation and blue-shift is expected if a decrease of the critical conjugation lengths takes place. Polymers with flexible chains or blocks make easier changes of conformation upon going from solution to films, but deeper studies involving the temperature dependence of the fluorescence emission should be required to confirm if this is the present case.

It can be affirmed however, that the blueshift may arise by the presence of, on average, shorter effective conjugation lengths, due to the freezing of conformational states during the fast solvent evaporation, to solvatochromic effects brought about by changes of both dielectric constant and refractive index of the medium, or to still to excitonic splitting originated by the presence of aggregates. No additional band is observed, as for example the β -phase of polyfluorenes [20,26,38] indicating that J aggregates are not formed. Also, we may consider that the excitonic splitting is small and the electronic bands of both the isolated and aggregated chains are strongly overlapped. Moreover, since the absorption spectra in solution lies in lower energy and are sharper, chloroform may be considered a good solvent for this polymer series inducing a more extended chain conformation in solution.

Steady-state emissions of the copolymers in the solid state are depicted in Fig. 5. Compared with the spectra in solution, all of them are red-shifted, they are not mirror images of the solid state absorptions and the bands are broader. In addition, all of these spectra have a higher intensity red-edge bands which are characteristic of aggregates. Aggregate emission of polymers in solid state is a common phenomenon [18–20,26,27]. The LaPPS30-0 emission band is

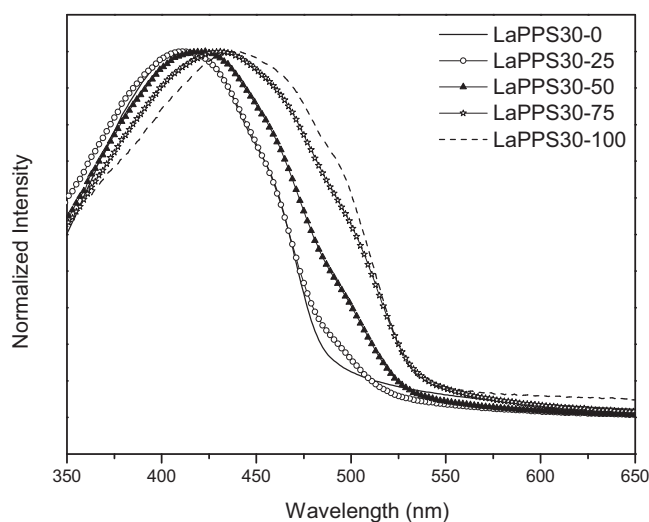


Fig. 4. Electronic absorption spectra of LaPPS30 series in the solid state.

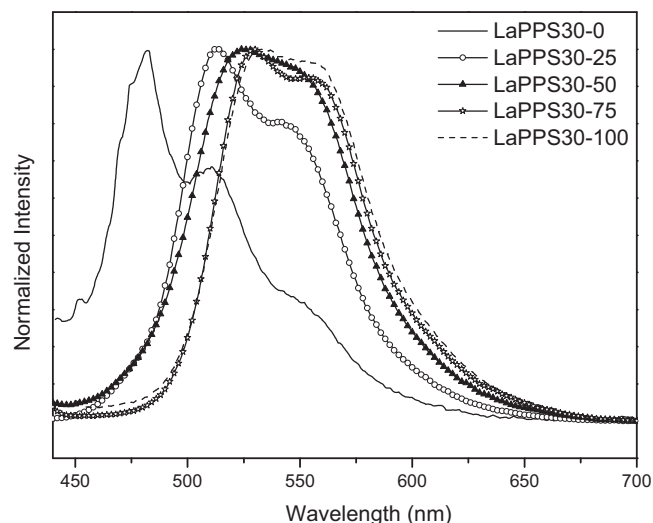


Fig. 5. Steady-state photoluminescence spectra of the LaPPS30 series in film form.

very similar in energy and vibronic structure as other polyfluorenes in [13,20] and some aggregation is evidenced by the red-edge tail around 550 nm. LaPPS30-100 in solid state also showed two vibronic emission peaks as in solution but they are red-shifted and with almost the same intensity. This indicates that aggregation is also occurring as observed for other polythiophenes [21–23,25,37].

LaPPS30-25 and LaPPS30-50 apparently show two emission bands: a weak blue-edge band arose around 474 nm whose intensity decreases with the increase of the thiophene content and a lower energy band whose peak position shifts to the red and relative intensity increases with the amount of thiophene. The photoemission of the copolymer LaPPS30-75 is indistinguishable of that of LaPPS30-100, as also observed in solution, indicating that if excited, those fluorene–vinylene units will transfer the energy to the thiophene–vinylene segments.

The fluorescence decays for films of all copolymers were also analyzed using exponential functions. Again, all of the samples were excited at 350 nm. As done for solutions, in the first set of experiments, the emission decay in the maximum of the emission band of each copolymer was recorded, and after, they were also recorded at lower energy.

LaPPS30-0 decay ($\lambda_{em} = 514$ nm) is biexponential, as it does in solution, with a faster component $\tau_{1PL} = 0.95 \pm 0.03$ ns (85%) and a slower component with $\tau_{2PL} = 4.7 \pm 0.02$ ns (15%). When the emission is followed at longer wavelengths ($\lambda_{em} = 525$ nm) the decays become faster suggesting that some kind of relaxation process is occurring.

The decay of the LaPPS30-100 films at $\lambda_{em} = 525$ nm is mono-exponential, as verified for solutions, with a $\tau_{PL} = 0.19 \pm 0.01$ ns (Table 4). However, differently from solutions, this decay is much faster, suggesting that this polymer in solid state is undergoing some kind of quenching process [39,40]. As the emission wavelength is red-shifted to 562 nm, the decay becomes biexponential with a faster component with $\tau_{1PL} = 1.46 \pm 0.08$ ns (88%) and a longer component with $\tau_{2PL} = 7.9 \pm 0.9$ ns (12%). The faster component is similar to others reported for polythiophenes (1500 ps) [41,42] but no longer component has not been observed in solution. Longer components for polythiophene decays are also reported and attributed to aggregates or excimers [37] but here we do not have further evidence for this.

The decay of LaPPS30-25 has a faster component (0.973 ± 0.08 ns) with a larger contribution (95%) and a slower one (13.9 ± 0.3 ns) (5%) as shown in Table 4, when the emission is collected at $\lambda_{em} = 514$ nm. The faster component is very similar to the faster one for LaPPS30-0 (0.95 ± 0.03 ns) suggesting that it is related to the fluorene–vinylene block. Nevertheless, the other component is much slower than any other observed for LaPPS30-25 solution. Slower decays in this time range is typical of excimeric/exciple species, which is also consistent with the broader and red-shifted band located at 545 nm in the PL spectrum (Fig. 5). When the decay is followed at $\lambda_{em} = 562$ nm the excimeric/exciple decay appeared with a greater proportion (10%) and the faster component (1.6 ± 0.2 ns) becomes similar to that observed for LaPPS30-100.

LaPPS30-50 and LaPPS30-75 decays ($\lambda_{em} = 525$ nm) were mono-exponential, with shorter lifetimes with increasing the thiophene–vinylene content (LaPPS30-50, $\tau = 0.598 \pm 0.009$ ns; LaPPS30-75, $\tau = 0.233 \pm 0.009$ ns). Nevertheless, they become bi-exponentials if they were followed at longer wavelengths ($\lambda_{em} = 562$ nm) emulating the behavior of LaPPS30-100. The collected data might indicate that two different species are contributing to the emission in solid state, one more isolated but interacting in the solid state and other more aggregated, with a larger contribution when emission is collected at longer wavelength [23]. For all of the copolymers, when the decay collected at $\lambda_{em} = 562$ nm, a slower component with lifetime in the range of

7.7–13.8 ns was observed, suggesting that aggregation is effectively occurring [23,42]. We observe in the PL spectra a lower energy band with relatively high intensity for all samples, which based on the lifetime determination, can be attributed to the excimer/exciple species or to pre-formed ground state dimers. Considering that no greater changes of the absorption spectra were noted, we may consider the possibility of excimeric/exciple species as the component emitting in longer wavelengths [42,43]. Moreover, since for both LaPPS30-0 and LaPPS30-100 there are two emissions, one due the isolated chains and the other to some type of aggregates, only a partial energy transfer processes from the higher energy emission to the lower energy species should occur. For the terpolymers (LaPPS30-25, 50 and 75), if the fluorene–vinylene groups were excited, there is a energy transfer from the fluorene–vinylene toward the thiophene–vinylene blocks leading to a predominance of the emission coming from this last block as its content increases. Aggregates in these copolymers emit in a completely different time scale, suggesting the presence of interchain excitons.

In general, in the absence of electron transfer processes, the occurrence of energy transfer in conjugated polymers may be ascribed to several mechanisms [16]. One of these is energy migration which is a very fast non-radiative process, occurring within few pico-seconds [44]. Since in the present work the time scale was much slower (lower limit was 90 ps), energy migration processes were not followed under the experimental conditions used. However, in addition to energy migration, other non-radiative energy transfer processes such as Förster mechanism are also expected for conjugated polymers [16,44–46]. Since there is a strong spectral overlap between the fluorene emission (PL) and the thiophene electronic absorption, the non-radiative energy transfer process by Förster (FRET) is possible. This mechanism induces simultaneous changes in two photophysical properties. One is the decrease of the donor (fluorene) PL intensity and the other is the decrease of the donor emission lifetimes. The efficiency of the FRET process may be determined by the expression:

$$\varepsilon = 1 - \frac{\tau_D}{\tau_D^0} \quad (2)$$

where τ_D^0 and τ_D are the lifetime of the donor in the absence (LaPPS30-0) and in the presence (LaPPS30-X) of the acceptor, respectively.

According to the lifetime data for both solutions (Table 3) and films (Table 4), the decays for LaPPS30-25 are longer than those for LaPPS30-0, which indicates that the FRET efficiency by Förster mechanism is not an important process. Although a deeper rationale for this result was not performed here there are some reports in the literature showing that energy transfer process from fluorene–vinylene copolymers to terminal oligothiophene groups are only efficient for oligomers with well defined sizes: for three to four units the FRET is more efficient than for oligomers with two repeating units or longer than four [47]. In other words, there are some structural hindrances, which favor FRET in copolymers of fluorene and thiophene, which may explain the absence of FRET for LaPPS30-25.

Using Eq. (2), the efficiency for FRET of LaPPS30-50 in solutions was calculated for the emission at 475 nm ($\tau_D^0 = 1.02$ ns and $\tau_D = 0.86$ ns, from Table 3) which gives $\varepsilon = 0.294$. This value is similar to that for the same sample in film measured at 525 nm ($\tau_D^0 = 0.95$ ns and $\tau_D = 0.598$ ns, from Table 4), which gives $\varepsilon = 0.233$. In addition, a stronger quenching is observed for LaPPS30-75, which in film gives $\varepsilon = 0.701$ and in solution the quenching is almost complete. Based on these data, we may conclude that the quenching efficiency of fluorene to thiophene blocks by Förster is higher for solutions than for solid state, probably due to the contribution of other process apart from Förster. Due to the non-available data for the size and size distribution of both fluorene and thiophene blocks

Table 4

Fluorescence decays of the LaPPS30 series in the solid state, using $\lambda_{\text{exc}} = 350 \text{ nm}$; B is the contribution of every lifetime to the entire decay, χ^2 measures the quality of the exponential fitting.

Materials	λ_{em}	τ_1 (ns)	B (%)	τ_2 (ns)	B (%)	χ^2
LaPPS30-0	514	0.95 ± 0.03	85	4.7 ± 0.2	15	1.105
	525	0.78 ± 0.02	81	4.07 ± 0.08	19	1.156
LaPPS30-25	514	0.973 ± 0.008	95	13.9 ± 0.3	5	1.148
	562	1.6 ± 0.2	90	12.2 ± 0.3	10	1.165
LaPPS30-50	525	0.598 ± 0.009	100	–	–	1.075
	562	1.42 ± 0.03	92	13.8 ± 0.3	8	1.187
LaPPS30-75	525	0.233 ± 0.009	100	–	–	1.095
	562	1.25 ± 0.02	93	11.8 ± 0.4	7	1.283
LaPPS30-100	525	0.19 ± 0.01	94	–	–	1.243
	562	1.46 ± 0.08	88	7.9 ± 0.9	12	1.254

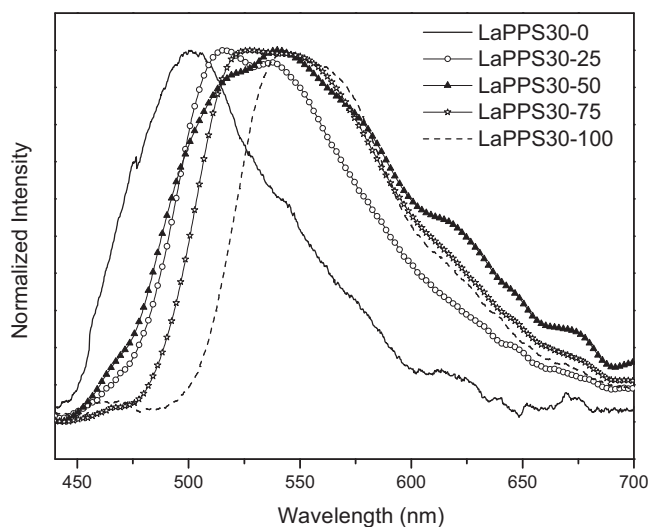


Fig. 6. Electroluminescence of the copolymers of the LaPPS30 series.

and to the complex description of the wavelength dependence with the size of both absorption and emission bands in the presence of energy transfer processes, we have not attempted to calculate the Förster radius for the FRET process. Nevertheless, Förster radius for FRET of thiophene–phenylene oligomers of different sizes has been reported to be in the range of 3.4–3.9 nm [48].

3.4. Electroluminescence measurements

Electroluminescence spectra of the ITO/PEDOT:PSS/LaPPS30-X/Ca/Al devices are depicted in Fig. 6. The EL emissions of the terpolymers LaPPS30-X, are in the same spectral range of the PL, but the emission profiles are different. The EL characteristics are compiled in Table 5. As a general description, emissions at longer wavelengths are relatively more intense in the EL than in the PL. For example, the emission intensity ratio is $I_{514 \text{ nm}}/I_{550 \text{ nm}} = 0.76$ (from Fig. 5) for the PL and is $I_{514 \text{ nm}}/I_{550 \text{ nm}} = 0.90$ (from Fig. 6) for the EL of LaPPS30-25. This behavior may be ascribed to the correlation between the higher efficiency of EL in the presence

Table 5

Electronic properties of the copolymers of LaPPS30 series.

Polymer	Turn-on voltage (V)	Luminance max. (cd/m^2)
LaPPS30-0	2.03	255
LaPPS30-25	2.18	188
LaPPS30-50	2.47	47
LaPPS30-75	2.06	137
LaPPS30-100	2.48	166

of aggregates or of more ordered regions in the polymer matrix. Comparing the PL in solid state and the EL of LaPPS30-0 (Fig. 6), we can see that the maximum of the EL is coincident with the band assigned to the aggregates. The higher energy band at 483 nm (Fig. 5) is present only in the PL. No vibronic structure is present in the EL. This behavior suggests that the excited state formed by the exciton recombination in the EL processes is occurring near the aggregates while the PL occurs by both, isolate chains and aggregates, as demonstrated by the emission decays. Trapping of isolated excitons by aggregates is a common phenomenon in electroluminescence of conjugated polymers [49]. PL resulted of the emissions from both zones, where the efficiency is a convolution of the absorptivity of these two regions and of the emission quantum yield of each one. Because in general the aggregate emission has lower quantum yield, the lower energy band has lower intensity.

In Fig. 7 the luminance vs. voltage data is shown. The turn-on voltage is practically the same for all materials, with values of 2.03–2.48 V. As one can see, there is not a straightforward correlation between the thiophene–vinylene content in the terpolymer and luminance, but what is clear is that the luminance is always lower in the presence of thiophene units compared to the LaPPS30. Thus, we may conclude that the thiophene component does not contribute to the device efficiency. The chromaticity diagram of the copolymers with their respective x, y coordinates is shown in Fig. 8.

The general trend followed by the main properties of the copolymers is displayed in Fig. 9, in function of the composition. The curves were normalized, taking the highest value as 1.0 and the

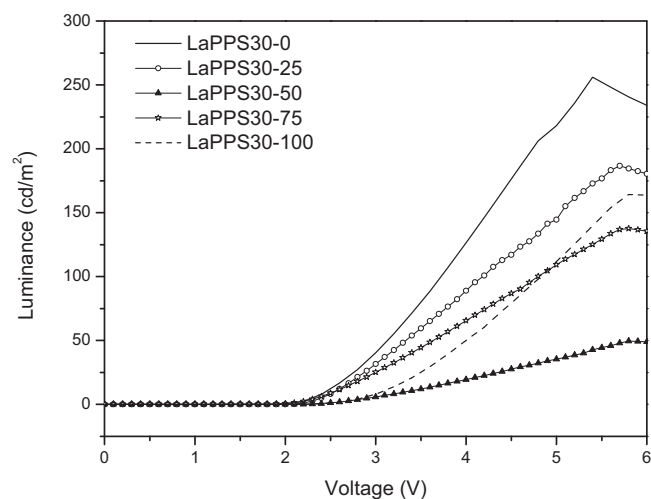


Fig. 7. Luminance vs. voltage for the LaPPS30 series in devices formed by ITO/PEDOT:PSS/LaPPS30-X/Ca/Al.

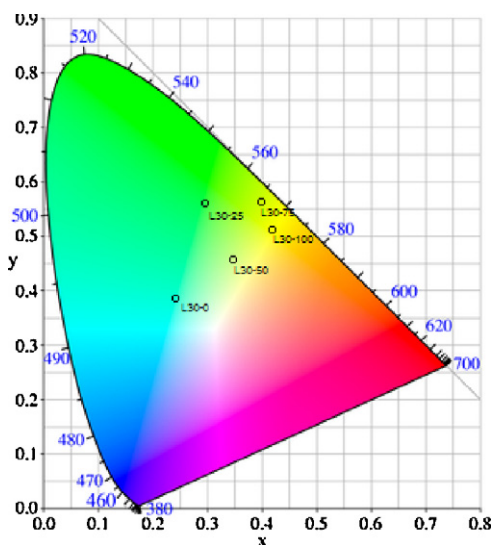


Fig. 8. Chromaticity diagram for the LaPPS30 series. LaPPS30-0(a) (0.25;0.38), LaPPS30-25(b) (0.30;0.55), LaPPS30-50(c) (0.36;0.45), LaPPS30-75(d) (0.40;0.56) and LaPPS30-100(e) (0.42;0.52).

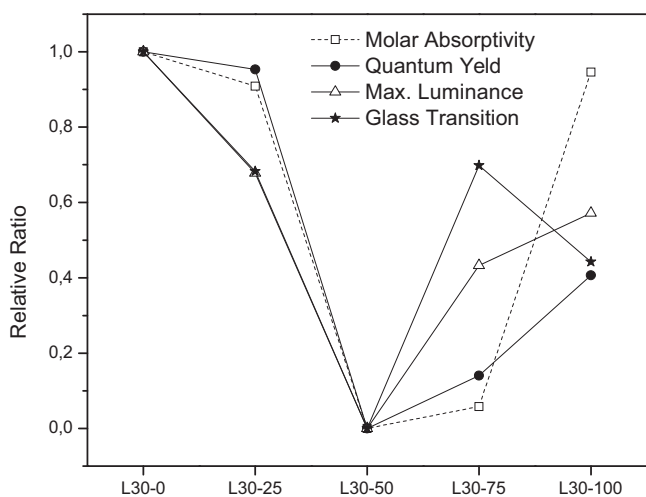


Fig. 9. Influence of composition on the general properties of the LaPPS30 series.

lowest as zero. The idea brought by this figure is that any property, optical, electronic or thermal depends on the size of building bricks: the highest properties are shown by LaPPS30-0, the copolymer without thiophene. With the progressive insertion of the thiophene containing blocks the properties decrease reaching a minimum when the ratio between components is near to the unity (LaPPS30-50) and with the further increase thiophenes containing units the properties began to rise again. It is possible that the aggregation of similar blocks lead to percolating paths for charge carriers and at the same time provided less free volume for macromolecular relaxations, explaining the decrease of the glass transition temperature for less blocked copolymer.

4. Conclusions

The photophysics data showed that the main issues in the photoluminescence mechanism of the copolymers can be ascribed to several simultaneous phenomena: emission from isolated (higher energy), excimer/excimer species and/or from pre-formed ground state dimers (lower energy); partial energy transfer processes from the higher energy emission to the lower energy

species; energy transfer from the fluorene–vinylene toward the thiophene–vinylene blocks leading to a predominance of the emission coming from this last unit as its content increases. Additionally, the dispersion in size and composition of the copolymers combined with different chain conformations will influence differently the intrachain energy transfer process. These associated species would lead to ordered zones, randomly distributed within a disordered matrix which formed an interconnected phase, similarly as bulk heterojunction in conjugated polymer blends. That morphology would provide percolating channels for the charge carriers to travel, facilitating recombination and exciton transport. Evidence for the trapping of isolated excitons by the ones formed in the aggregated sites was provided by the detection of the EL signal only at the lower energy side of the spectra, for all copolymers.

The main issue affecting thermal, photo- and electroluminescence properties was the macromolecular aggregation of similar blocks. As the copolymer LaPPS30-50 was prepared with 50% of each component, the random linking of dissimilar monomeric units hindered the blocked structure and its properties fell out of the tendency observed for all the other, such as molar absorptivity, quantum yield, lifetimes, maximum luminance, and LED turn on voltage.

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